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THE RELATION BETWEEN REDWOOD SECONDS AND KINEMATIC VISCOSITIES.*

By Guy Barr, B.A., D.Sc.

Synopsis.

This paper gives an account of a research undertaken with the object of revising the formula for converting Redwood seconds to kinematic viscosities, which was first prepared in 1913. The programme of work was arranged by the Viscosity Panel of the Institution of Petroleum Technologists, a series of twelve oils of suitable viscosities being used. As the result of this investigation it was found that the relation cannot be expressed by any single linear formula.

I. Introduction.

An equation for the conversion of Redwood seconds T to kinematic viscosities ν was obtained by Higgins in 1913 [1] by comparing the data obtained in a Redwood and in an absolute viscometer for eight oils at various temperatures between 10° C. and 60° C. His equation

$$\nu = AT - B/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where $A = 0{\cdot}00260$ and $B = 1{\cdot}715$) was accepted for many years without serious question, although Herschel [2] gave practical and theoretical reasons for preferring a value of 1·88 for B. Barr [3] found that the kinematic viscosity of a certain oil was 4 per cent. lower than that calculated from the Redwood time by means of this equation, and attempted to reduce the discrepancy by showing that Higgins' data might be made to give a value $A = 0{\cdot}00255$ if the results obtained with one oil were omitted as being liable to error owing to thermal hysteresis. Several other values for A and B have been proposed, which are tabulated by Garner and Kelly,[4] but it does not appear profitable to discuss any that refer to instruments constructed before 1924 and not directly compared with viscometer No. 1307, which was used by Higgins in deriving equation (1) and has been adopted as a standard of reference.[5] Since 1925, instruments submitted to the National Physical Laboratory have been compared with the standard at a Redwood time of *ca.* 350 seconds: since 1930 a second comparison at *ca.* 70 seconds has been included in the certification, so as to allow some estimate to be obtained of the variation of both A and B from the constants applicable to the standard.

Garner and Kelly [4] have recently put forward evidence to show that a single conversion equation is not adequate for the treatment of data obtained with their Redwood viscometers, and have deduced approximate values for the constants of two equations which are suggested as applicable

* Work carried out at the National Physical Laboratory for the Institution of Petroleum Technologists. Paper received March 11th, 1935.

to instrument No. 1307. The equations proposed are both of the same form as (1), but the constants indicated are

$$A = 0{\cdot}00260,\ B = 1{\cdot}79 \text{ for } T \text{ between 34 and 100}$$
$$A = 0{\cdot}00247,\ B = 0{\cdot}5 \text{ for } T \text{ greater than 100.}$$

A similar pair of equations, with appropriate constants, was shown to be capable of representing calibration data for the Saybolt viscometer; it was found by the A.S.T.M. Committee on Viscosity Standards [6] that two equations—at least—were necessary for this instrument. On behalf of the I.P.T., work has now been carried out at the National Physical Laboratory to ascertain whether more than one equation is actually required for the reference Redwood viscometer No. 1307 and to determine the constants.

II. Plan of Work.

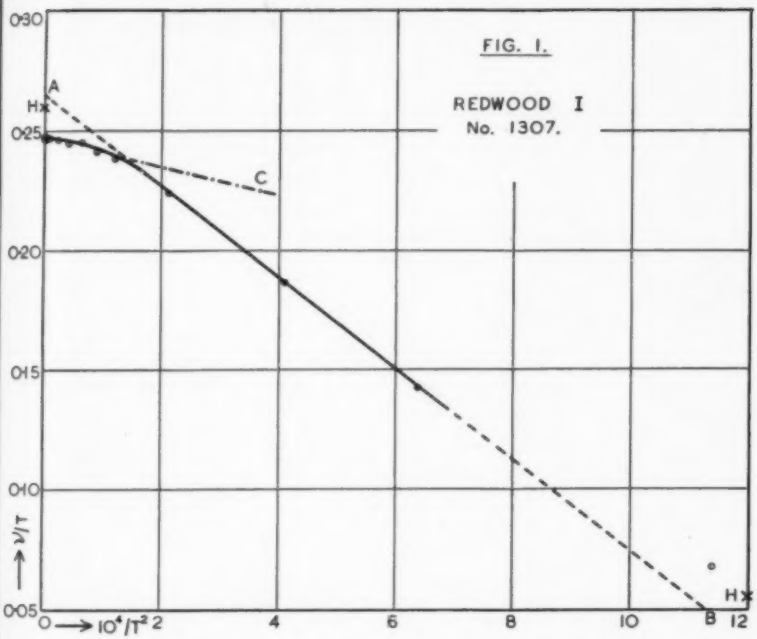
The programme arranged by the Viscosity Panel of the Institution of Petroleum Technologists required the determination of the Redwood times in No. 1307, and of the kinematic viscosities of a series of petroleum products at 70° F. It was recognized that results obtained at oil temperatures considerably above that of the room would probably be affected by cooling of the jet and base of the Redwood cup, and by contraction of oil in the recipient flask, but it was decided that these factors should be left for a later study. Eleven samples were furnished by Dr. Garner, blended to give Redwood times at 70° F. of approximately 30, 40, 50, 70, 90, 105, 120, 150, 200, 1000 and 3000 seconds, and the gap between 200 and 1000 seconds was bridged by means of a sample of 320 seconds viscosity that is used in the routine comparison of viscometers, submitted for test, with No. 1307.

III. Experimental Methods.

The Redwood times were determined in No. 1307 in accordance with the specification laid down by the I.P.T. The temperature of the room was adjusted to 70° F. $\pm$ 0·5° F. before each run, and under these conditions it was not difficult to keep the temperature of the water-bath constant to 0·2° F. and that of the oil to 0·1° F.

Kinematic viscosities were determined in three U-tube viscometers (Nos. 2, 3 and 4) constructed and calibrated in accordance with British Standard Specification No. 188—1929. The calibration depends on a knowledge of the viscosities at 25° C. of sugar solutions, approximately 40 per cent. and 60 per cent., of which the densities have been accurately measured. The interpolation formula and the corresponding tables (Appendix V) in this specification were derived from measurements made by Bingham and Jackson in 1917.[7] The substantial accuracy of the method was demonstrated by Barr,[3] who found that the calibration constant of a certain No. 3 U-tube derived from observations with a 60 per cent. sugar solution agreed within 0·3 per cent. with the constants deduced (*a*) by means of oils the (" absolute ") viscosities of which had been measured in a capillary tube viscometer of accurately known dimensions, (*b*) by " stepping-up " from Bingham's value for water via a No. 1 and a No. 2 U-tube viscometer, and (*c*) by " stepping-down " via a No. 4 viscometer from the

viscosity of a syrup–glycerol mixture determined by the falling-sphere method. Confidence in the application of the interpolation formula has since been gained by the consistency with which solutions made up from sugar of different grades of purity, and having densities varying even beyond the extremes included in the tables, have yielded the same calibration constant for a given tube. The thermometer used for the thermostat bath in which the U-tube viscometers were clamped was the same as that on which the oil-cup temperatures were noted in the Redwood tests : the bath was maintained at 70° F. ± 0·02° F.



For purposes of reference, and also to allow the calculation of dynamic viscosities if necessary, the densities of all samples at 70° F. were determined in a 50-ml. specific-gravity bottle.

IV. Data for a Calibration Curve.

The results are set out in Table I, which includes also the values of ν/T and of $1/T^2$ calculated from them for the purpose of plotting in a Higgins diagram. The unit adopted for ν is the centistokes; this system has the merit of avoiding many ciphers, and the values of A and B obtained from the plot will be in cs./sec. and cs. sec., respectively. The actual points are plotted in Fig. 1; a continuous curve drawn through them would be similar to that obtained by Garner and Kelly. It is obvious that no one straight line will pass satisfactorily near to all the points,

or even to all the points other than that for $T = 29{\cdot}6$. There is plenty of evidence to suggest that this point relates to a type of flow which differs from that at higher values of T, since Higgins, Herschel, and Garner and Kelly agree in finding that a linear equation fails to hold below about $T = 35$ sec. and calculations based on the theoretical and practical work of Boussinesq and of Schiller (see Appendix) indicate that when the viscosity is below that corresponding with $T = 38$, there is not time for the normal distribution of velocities in the cross-section of the liquid column to be attained before the liquid leaves the viscometer.

Va. Inadequacy of Linear Equations.

If the point corresponding with $T = 29{\cdot}6$ be disregarded, the data may be represented, with no discrepancies exceeding 0·002 cs./sec. by means of two equations,* both of the same form giving ν/T in cs. per sec. :—

$$\nu/T = A - B/T^2, \text{ where } \begin{cases} A = 0{\cdot}264,\ B = 189 \text{ for } T \text{ less than } 91 & (2a) \\ A = 0{\cdot}247,\ B = 50 \text{ for } T \text{ greater than } 91 & (2b) \end{cases}$$

Equation 2*a* is represented on Fig. 1 by the straight line AB, equation 2*b* by the continuation of the straight line C. (A straight line joining the points HH would represent Higgins' equation.)

Table I.

T.	$10^4/T^2$.	ν.	ν/T.	ρ.	ν/T calc.*
29·60	11·413	2·013	0·0680	0·8166	(0·0482)
39·61	6·374	5·640	0·1424	0·8166	0·1436
49·21	4·130	9·171	0·1864	0·8294	0·1859
68·70	2·119	15·37	0·2237	0·8437	0·2239
89·22	1·256	21·27	0·2384	0·8516	0·2386
104·15	0·921	25·10	0·2410	—	0·2425
123·0	0·661	30·14	0·2451	0·8576	0·2445
149·5	0·447	36·60	0·2448	0·8604	0·2453
202·1	0·245	49·69	0·2459	0·8651	0·2455
319·4	0·098	78·91	0·2471	0·8893	0·2460
994·6	0·010	245·5	0·2469	0·8773	0·2469
2992	0·001	738·4	0·2468	0·8841	0·2470

* Calculated by formula $\nu/T = (0{\cdot}264 - 189/T^2)\left\{1 - 0{\cdot}0644/10^{\left(\frac{87{\cdot}5}{T}\right)^3}\right\}$.

Although these equations may be useful for practical purposes, their adoption cannot be justified except for convenience in approximation. In the first place, it is possible to draw a smooth continuous curve which passes so close to all the points (other than $T = 29{\cdot}6$) that no value of ν/T read from it differs by as much as 0·001 cs./sec. from the experimental value : the individual determinations are probably subject to an error of this order. In the second place, if two such equations held accurately, each over a wide range of times of flow, it would be necessary to postulate the occurrence of different regimes above and below $T = 91$. Dr. Broom suggested that the

* These formulæ have been slightly modified in the equations given in "Standard Methods for Testing Petroleum and its Products," 3rd Edn. 1935, p. 170.

critical region might be studied by means of observations of the rate of flow at different stages during the discharge of an oil of appropriate viscosity from the Redwood cup. Knowing the area of cross-section of the cup, the fall in head may be calculated from the total volume that has run out at any time so long as the level remains in the cylindrical part of the cup. Then if the head at any time be h,

$$\nu = kh\,dt/dh - c\,dh/dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k and c are constants so long as an equation such as (1) holds. If the second term on the right be small compared with the first and the falls in head Δh during an interval Δt be small compared with h, little error will result by substituting $\Delta h/\Delta t$ for dh/dt in equation (3) and taking for h the arithmetic mean of the heads before and after the fall Δh. Thus if ν be constant, a plot of $h\Delta t/\Delta h$ against $\Delta h/\Delta t$ should give a straight line of slope $\tan^{-1} c/k$, intersecting the axis of ordinates at $h\Delta t/\Delta h = \nu/k$.

Vb. Study of the Transitional Region.

The experimental procedure that was tried for the purpose of testing the method was to provide a series of seven weighed beakers in which to collect the oil discharged during various intervals. An oil giving $T = 123$ sec. was used, and the recipient beaker was changed after 20, 45, 80, 110, 150, 200 and 260 seconds: the operation of replacing one beaker by the next could be carried out without losing any oil, although there was naturally an error approaching 0·2 sec. in defining the time intervals. The density of the oil was determined at the temperature (70° F.) prevailing in the cup, so that the volumes collected could be calculated from the increases in mass Δw of the beakers. Instead of working out the successive mean heads h from the heads h_{n-1} and $h_n = h_{n-1} - \Delta w/(\rho S)$ at the beginning and end of each interval (S = area of cross-section of the cup), it was found more convenient to leave the results in terms of mass throughout. If we put $H = h\rho S$, we shall have $H_1 = h_0\,\rho S - \frac{1}{2}\Delta w$, and so on, and the Poiseuille–Knibbs equation may be rewritten in the form

$$H\Delta t/\Delta w = 8\nu LS/(\pi a^4 g) + m\Delta w S/(\pi^2 a^4 \Delta t \rho g) \quad . \quad . \quad . \quad (3a)$$

In practice, H (or h) requires to be reduced by applying a small "logarithmic head" correction (Meissner's formula), giving a more accurate value H'. Further, the area S is normally equal to the area of cross-section of the cup minus that of the thermometer, but during the last interval the thermometer bulb was uncovered, so that a different value of S had to be used in calculating the fall of H. The following table gives the experimental data and the expressions calculated therefrom: the column headed W shows the total number of grammes of oil run out up to the middle of the interval concerned.

When the above values of $H'\Delta t/\Delta w$ were plotted against $\Delta w/\Delta t$, the points were found to lie as nearly as could be expected on a straight line; the maximum divergence occurred for the point corresponding with the unintentionally short fourth interval which lay 1·6 units (= 0·8 per cent.) below the line. The equation to this line is

$$H'\Delta t/\Delta w = 204{\cdot}5 + 29\Delta w/\Delta t \quad . \quad . \quad . \quad . \quad (3b)$$

TABLE II.

Temperature 70° F. : viscosity of oil, 123 Redwood seconds.
Initial head $h_0 = 8{\cdot}964$ cm. (to bottom of jet).
Area of cross-section of cup 16·98 cm.², of thermometer 0·28 cm.² : $S = 16{\cdot}70$.
Apparent density of oil, $\rho = 0{\cdot}850$ gm./cm.³.
$H = h_0\,\rho S - W = 127{\cdot}29 - W$.

Interval	Δt.	Δw.	$\Delta w/\Delta t$.	W.	H.	H'.	$H'\Delta t/\Delta w$.
1	20	11·055	0·5527	5·527	121·76	121·68	220·0
2	25	12·591	0·5036	17·350	109·94	109·82	218·0
3	35	15·408	0·4402	31·350	95·94	95·73	217·5
4	30	11·581	0·3860	44·844	82·45	82·32	213·2
5	40	13·107	0·3277	57·187	70·10	69·90	213·4
6	50	13·392	0·2678	70·436	56·85	56·69	211·8
7	60	12·519	0·2086	83·392	44·00	43·70	209·2

Identifying this with equation (3*a*) we have

$$mS/(\pi^2 a^4 \rho g) = 29$$

The value of a, the mean radius of the jet, cannot be measured with any great accuracy in this instrument, but may be obtained from the $A = 0{\cdot}264$ of equation (2*a*), which represents the value of $\pi a^4 h_m g/8VL$ in the Poiseuille equation. We thus find

$$\begin{aligned} m &= 29\pi^2 a^4 \rho g/S \\ &= 29\pi A \rho 8 VL/(h_m S) \end{aligned}$$

where h_m is the logarithmic mean head in the normal use of the viscometer : for this instrument $h_m = 7{\cdot}36$ cm.

Now, since we have found m to be substantially constant in the range covered by the above experiment, an equation of the same type as (1) should also hold, in which $B' = mV/8\pi L$. The value for B' for this range is, therefore,

$$B' = 29A V^2 \rho / h_m S,$$

whence

$$B' = 132 \text{ cs. sec.}$$

If the calibration curve based on Table I is actually continuous, this value of B' should be approximately equal to that obtained by drawing a tangent to the curve at a point corresponding with the mean of the range involved. To find the values of $1/T^2$ on the Higgins diagram that correspond with the first and last intervals of Table I, we must note that T defines a certain (average) condition of flow through the jet which must be a function of the Reynolds number. The Reynolds number R is inversely proportional to νT, *i.e.* to T^2 as a first approximation. If the rate of flow is varied while ν is constant, as in this experiment, the Reynolds number will vary between $R_1 = RT/(50\rho) \times (\Delta w/\Delta t)_1$ and $R_7 = RT/(50\rho) \times (\Delta w/\Delta t)_7$, and the values of T_1 and T_7 that would correspond with these values of Reynolds number in normal use would be given by

$$T_n^2 = T^2 R/R_n = 50\rho T/(\Delta w/\Delta t)_n.$$

Taking $(\Delta w/\Delta t)_1 = 0{\cdot}5527$ and $(\Delta w/\Delta t)_7 = 0{\cdot}2086$ we find $1/T_1^2 = 1{\cdot}33 \times 10^{-4}$ and $1/T_7^2 = 0{\cdot}502 \times 10^{-4}$ on $T_1 = 87$, $T_7 = 141$. The tangent to the curve at $1/T^2 = 0{\cdot}91$ was found to give $B' = 100$ cs. sec. approximately.

The difference from the value $B' = 132$ deduced in the last paragraph appears rather large in view of the probable errors, but may probably be explained by uncertainty in the value of h_0 (see Section VI).

A more critical test for the occurrence of a change of regime is probably provided by observation of the form of the issuing stream of oil. The oil wets the lower surface of the agate, and the stream contracts, more or less rapidly according as the flow is fast or slow, into a nearly cylindrical jet, which finally becomes so attenuated that it breaks up into drops and spray. The distance from the agate to the point at which the transition occurs may be seen to diminish steadily as the oil-cup empties: with a 120-second oil the distance decreases from about 20 cm. to 5 cm., and with a 70- or 90-second oil the unbroken lengths are greater, but in no case has any sudden change been observed.

Oils of much higher viscosity give a short jet when the flow is started, and a succession of large drops breaking off from a pendant drop when the level in the cup has fallen: this transition does not correspond with any observable change of slope in the calibration curve.

VI. Suggested Nature of the Increased Resistance at High Viscosities.

Assuming, then, that the calibration curve is continuous, it is natural to attempt to find an equation that will satisfy the curve, and to suggest some sort of physical explanation of the behaviour. It appears probable that the increased resistance to the flow at high viscosities should be due, in some manner, to the form of the liquid stream where it leaves the viscometer. The issuing liquid has to flow within an oil–air interface the shape of which obviously depends on the viscosity, and presumably also on the surface tension of the oil: the surface tensions of oils do not, normally, vary over any wide range. For Redwood times up to about 100 seconds the stream contracts very rapidly, within a few mm. of the agate jet, to an approximately cylindrical form: the more viscous the oil the more gradual is this contraction. Without attempting to analyse the equilibrium between the forces due to surface tension, to gravity, and to viscosity at different rates of flow, it seems probable that the more or less stagnant outer layers of the converging portion of the stream constitute a virtual extension of the capillary tube, so that energy is here dissipated in work done against viscous forces. This suggestion requires that the pressure at the axis be greater than atmospheric in this region; although no excess as great as $30/0{\cdot}5 = 60$ dynes per cm.^{2} can exist in the oil at the periphery (assuming 30 dynes/cm. as the surface tension of the oil and 1 cm. as the external diameter of the agate jet), the pressure at the axis must be greater than at the periphery if there is some radial flow.

The usual Couette correction applied to viscometers with submerged discharge increases the length of the capillary by 0·6 time its radius to allow for the convergence of the streamlines at the entrance: an additional increase of the same amount has been supposed to occur at the exit when the issuing stream diverges freely into an infinite volume of liquid. To reconcile the value $B = 189$ obtained experimentally for T less than 90 with the theoretical expression $B = mV/8\pi L$, it is necessary, if m be taken

as equal to 1·1, to assume that $L = 1{\cdot}158$ cm. The measured length of the jet is 1·024 cm., so that, if the Couette correction for the entrance is $0{\cdot}6 \times 0{\cdot}080 = 0{\cdot}048$ cm., the correction for the exit end would need to be 0·086 cm., or 1·1 times the radius. If we assume that the correction for the exit end is a function of the viscosity (and surface tension) of the oil, and may amount to as much as 2·6 times the radius when the flow is very slow, we have a not improbable explanation of the form of the calibration curve. The virtual length of the capillary is then to be taken as $1{\cdot}024 + 0{\cdot}134$ cm. at low viscosities and as $1{\cdot}024 + 0{\cdot}211$ cm. at high viscosities.

Incidentally, the occurrence of a large Couette correction for the exit end would require that the effective head of the oil should be measured as the height of the filling point above the " virtual " end instead of the actual end of the capillary. In the calculation of the coefficient m from the experimental data of Table II the value obtained becomes lower if h_0 be supposed greater by a fixed amount, and it will be still lower if, as we assume, h_0 increases as the rate of flow decreases. If h_0 increases over half the range between $8{\cdot}964 + 0{\cdot}086$ cm. and $8{\cdot}964 + 0{\cdot}163$ cm. during the experiment for which data are given in Table II, the value calculated for B' would be considerably below, instead of above, that indicated by the tangent to the calibration curve.

This suggestion as to the nature of the increase in resistance offered to the flow of oils of high viscosity is implicit in an equation which has been devised to express the calibration curve. The constants A and B of an equation such as (1) may be regarded as evaluations of two terms in the Poiseuille equation, each of which involves the " virtual length " of the capillary in the denominator. If the virtual length tends towards a constant value $l + n_0 a$ at high rates of flow and becomes $l_0 + xa$ at a Redwood time T, where x is a function of the Reynolds number and surface tension, then ν/T will be equal to

$$(A - B/T) \times \frac{l + n_0 a}{l + xa}$$

where A and B are the constants holding for low values of T. The correcting factor may be written as $(1 - f)$, where f is a function of T only if we ignore the differences of surface tension. The experimental determinations (other than $T = 30$) and the smooth calibration curve drawn through the points plotted on a Higgins diagram are reproduced with an error of less than $\pm$ 0·001 cs./sec. in ν/T by the following formula, in which f has been expressed in an exponential form :—

$$\frac{\nu}{T} = \left(A - \frac{B}{T}\right)(1 - f)$$

where $A = 0{\cdot}264$ cs./sec.
$B = 189$ cs. sec.

$$f = 0{\cdot}0644 \times 10^{-\left(\frac{87{\cdot}5}{T}\right)^2}.$$

The formula is naturally independent of the assumptions that have been made as a guide to the nature of the correction term.

The above equation, as also the approximate equation (2a), is valid down

to $T = 40$, but no data have been obtained to fix the form of the curve at shorter times except for one point, $T = 29{\cdot}6$, which lies considerably above the straight line drawn through the points $T = 40$, 50 and 70. A breakdown of any simply corrected Poiseuille equation is to be expected below $T = 38$ (see Appendix), and Schiller has shown that correct values for ν/T may be obtained from observations made with a short-tube viscometer if the coefficient m be given values determined by other experiments. It appears to be wrong to ascribe the breakdown to turbulent flow, since the Reynolds number corresponding with $T = 29{\cdot}6$ is only about 610, which is much below the value required for turbulent flow even in long tubes. The curve should, therefore, be continued in a direction such that if no further change of regime occurred the point corresponding with $\nu/T = 0$ would lie on it: if the mean radius retained the value calculated from $A = 0{\cdot}264$ cs./sec., a liquid of no viscosity would give T 18·7. Hence a curve passing through the two points $\nu/T = 0$, $10^4/T^2 = 28{\cdot}7$ and $\nu/T = 0{\cdot}0856$, $10^4/T^2 = 11{\cdot}41$, and becoming indistinguishable from the straight line given by $\nu/T = 0{\cdot}264 - 189/T^2$ at about $T = 38$, should give an approximation to the correct one until turbulent flow occurs in the jet (probably at a Reynolds number greater than 3000, say $T = 20$). Such a curve would be obtained by adding to the normal equation a factor

$$\left\{1 - 10^{-\left(\frac{T}{30}\right)^{5\cdot 6}}\right\}$$

multiplying the B term, but we have not determined further points which would be necessary to justify the inclusion of such a factor in the general equation.

APPENDIX.

CALCULATION OF A LOWER UNIT LIMIT FOR THE APPLICATION OF A FORMULA OF THE POISEUILLE TYPE.

Boussinesq and Schiller have shown by calculation and by measurement that the value of the coefficient m of the kinetic-energy term of the Poiseuille equation will begin to decrease when $R = 33l/d$, where l and d are the length and diameter of the capillary and R is the Reynolds number. The Reynolds number corresponding with a rate of flow of $50/T$ ml. per sec. is given by $R = 200/(\pi d\nu T)$: hence the maximum value of R permitted will be that corresponding with ${}_0T_0 = 6/(\pi l)$, whence, assuming $A = 0{\cdot}00264$, $B = 1{\cdot}89$, $l = 1{\cdot}024$, we find $T_0 = 37{\cdot}7$. Actually the value of R is greatest at the beginning of the run, so that if the maximum is not to be exceeded at any time, T_0 must be supposed greater than 37·7. The more accurate calculation involves solution of equation (3) as a quadratic in dh/dt, and leads to the value $T_0 = 38{\cdot}5$, so that the error is not serious.

The curve given by Schiller and Kirsten [8] indicates that when R has increased to $100l/d$ the coefficient m will have decreased to 8/9 of its normal value. If we reduce B of equation (2a) to $B' = 168$ cs. sec. we shall have $T^2 = (\nu T + B')/A$, giving $T = 29{\cdot}55$ as the time of flow corresponding with $R = 610$ or with $\nu T = 62{\cdot}1$ cs. sec.: hence $\nu/T = 0{\cdot}0712$ cs./sec., at $T = 29{\cdot}55$, whereas the normal value $B = 189$ would give $\nu/T = 0{\cdot}0473$.

The divergence agrees very closely with that of the experimental point for $T = 29{\cdot}6$ (Table I) from the straight line of equation (2*a*) : the curve above mentioned could, therefore, be used to supply values for ν/T between $T = 40$ and $T = 30$ seconds.

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REDWOOD-KINEMATIC RELATIONSHIPS AT 70° F., 140° F., AND 200° F.

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Introduction.

The use of kinematic viscosity for the expression of the viscosity of petroleum products is being more widely adopted year by year as an alternative or addition to the present methods which involve commercial viscometers such as the Redwood, Saybolt or Engler. At the World Petroleum Congress, 1933, a resolution was passed recommending the expression of viscosity in kinematic units, although provision was also made at the same time for the use of dynamic viscosity units, *i.e.* poises, if desired. In view of the widespread adoption of Viscosity Index as a measure of the viscosity–temperature relations of lubricating oils, it has been found that the readings with the Saybolt instrument—on which Viscosity Index is based—are not sufficiently accurate, with oils of low viscosity, for commercial requirements, and there has recently been published in the United States a number of papers investigating the possibilities of the wider use of kinematic viscosity.

These recent articles indicate that attention is being directed towards the use of viscometers capable of more accurate control than the commercial instruments of the Saybolt or other types. As a first step towards the adoption of kinematic viscosity, it is, however, essential that means shall be available for the accurate inter-conversion of viscosities measured in the Redwood, Saybolt and Engler viscometers, and true viscosity expressed in centistokes.

In the present paper, work is described with the Redwood No. I viscometer, with the object of providing conversion data from standard Redwood seconds to kinematic viscosities at temperatures of 70° F., 140° F., and 200° F. In the third edition of "Standard Methods for Testing Petroleum and its Products," as a result of work carried out by Dr. Barr at the National Physical Laboratory, the Institution of Petroleum Technologists has adopted equations for the conversion of Redwood viscosity to kinematic viscosity, which are accurate to $\pm$ 1 per cent. for Redwood outflow times at 70° F. It was found in the course of the investigation described in the present paper that the same factors do not apply at 140° F. and 200° F. as at 70° F., and this is no doubt in part due to one feature of the design of the Redwood No. I instrument, namely, that the base of the oil cup itself is exposed to atmospheric temperature. As a result of this work, it was considered necessary to develop equations which would cover the whole range of viscosity for each of these temperatures, and to facilitate the use of these formulæ, skeleton conversion tables have been prepared. The kinematic

viscosities so calculated from Redwood viscosities are, it is believed, accurate to $\pm 0{\cdot}5$ per cent., but the determination of kinematic viscosity via the Redwood viscometer will also be subject to the experimental error of the Redwood viscometer, *e.g.*, $\pm 0{\cdot}5$ per cent. to ± 1 per cent.

As has been pointed out previously, it is felt that any general adoption of kinematic viscosity must be preceded by a time in which kinematic viscosity and Redwood or other viscosities are used side by side, and it is the purpose of this paper to furnish data which will be of some service towards the more general adoption of kinematic viscosity.

Previous Work.

Considerable work has been carried out upon the relationships between the " time of efflux " and kinematic viscosity for the Redwood No. I viscometer, but, in the main, this has been concerned with temperatures at, or about, 70° F. The pertinent data have been summarized and analysed by Garner and Kelly.[1] Waidner,[2] in 1915, gave conversion tables for the Saybolt Universal, Engler and Redwood viscometers, and stated that, whereas the Saybolt–Engler conversion factors varied only with oil viscosity, the Saybolt–Redwood factors varied both with viscosity and with temperature. The variation was such that the ratio obtained by dividing the Saybolt times by the equivalent Redwood times was greater at low temperatures than at higher temperatures. This would indicate that at higher temperatures, either the Redwood or Saybolt instrument (or both) give efflux times which do not bear the same relation to kinematic viscosity as do similar efflux times obtained at lower temperatures; Waidner suggested, as a reason for this difference, that the jet temperature in the Redwood viscometer was below that of the nominal test temperature, when the latter was, for example, 200° F. Savill and Cox[3] have published data referring to efflux times from a No. I Redwood instrument at temperatures ranging from 15·5° C. to 150° C., but most of the results refer to temperatures of 50° C. and above. The data are not very precise, but do indicate that at the higher temperatures the value of A in an equation of the type :

$$\text{Kinematic viscosity} = AT$$

where T equals Redwood efflux time in seconds, is smaller than at lower temperatures.

In the present work, the relationships between kinematic viscosity and Redwood No. I outflow times have been investigated, using an N.P.L.-certified Redwood No. I viscometer, at temperatures of 70° F., 140° F. and 200° F. At the time this work was conducted, the second edition (1929) of the I.P.T. " Standard Methods " was in force, and the work reported in this paper was, therefore, carried out, such that all conditions laid down in Serial Designation L.O. 8 were met. This included the insulation of the receiving flasks when testing at temperatures of 140° F. and 200° F., which procedure, in the recent third edition (1935), has been abandoned. It has been possible, however, to obtain an experimental correction curve which allows the conversion of results obtained with insulated flasks to those which are obtained according to the most recent procedure.

The relationships between kinematic viscosity and outflow times at

both 140° F. and 200 F. would not be expected to agree with similar relationships determined at 70° F. for the following reasons: First, the oil which collects in the receiving flask at higher temperatures is cooled below the nominal test temperature, and thus a volume of oil, which is greater than 50 ml. at the nominal test temperature, is actually timed. Secondly, the agate jet of the Redwood No. I viscometer is not entirely surrounded by the heating medium, and at high temperatures must undoubtedly—at least for part of its length—be below the nominal test temperature. Both these factors tend to give increased times of flow at higher temperatures of test, and hence, in relation to true kinematic viscosity, the value of the A constant in the equation

$$\nu = AT,$$

must be smaller at temperatures of 140° F. and 200° F. than at 70° F. This has been found to be the case.

Experimental.

The Redwood No. I viscometer used in this work, No. 3967, was certified by the National Physical Laboratory as complying with the 1929 specification of the I.P.T. It also conforms in all essential details to the 1935 specification and has recently been compared at a series of viscosities (at about 70° F.) with standard viscometer No. 1307 at the National Physical Laboratory. The receiving flasks and thermometers had also been calibrated by the National Physical Laboratory.

In practice, Redwood viscosities were run at least twice, but usually three and sometimes four times, on each oil, depending on its actual viscosity. The mean values are recorded, and in all cases the bath liquid was water. U-tube viscometers (B.S.I. Specn. 188—1929) calibrated by the National Physical Laboratory were used to determine the kinematic viscosities of the oils. For the results at 140° F., a thermostatically controlled electrically heated water-bath was used, fitted with double stirring arrangements. This bath was approximately 15 in. long, 9 in. wide and 11 in. high, with the longer sides of glass. The thermo-regulator used kept the bath temperature constant, to within readable limits on the thermometer, which was the same one as was used in determining the Redwood viscosities. The identical thermometer was used in both determinations in order to minimize any errors due to thermometer differences. Moreover, both the Redwood and kinematic viscosities for any one oil were determined within an interval of one week. For the kinematic viscosities at 200° F., a beaker of about 5 litres capacity was used, with a good transformer oil as the bath liquid. Electrical heating was used as before, but hand control of an adjustable rheostat in the immersion heater element circuit was used to maintain the desired temperature. With care, this proved satisfactory, as four or five runs were carried out on each oil at 200° F. The substitution of water for transformer oil as bath liquid for the experiments at 200° F. gave identical results, but was not so convenient in use. As before, the same thermometer was used in determining Redwood and kinematic viscosities.

For results at 70° F., the thermostat was used, with water as the bath

liquid. All times of outflow were obtained using two stop-watches which had been checked against the Greenwich time signal and a synchronous electric clock, and for times longer than one minute it is believed that a high order of accuracy was obtained. The number of oils examined at 140° F. was thirteen, and ranged in viscosity at this temperature from 4·94 to 236·3 centistokes, corresponding to Redwood No. I outflow times of 39·8 and 973·3 seconds; at 200° F., fourteen oils were also examined, ranging in viscosity from 4·40 centistokes to 83·1 centistokes, *i.e.* 38·5 to 348·1 Redwood No. I seconds, whilst at 70° F. eight oils covering the range

TABLE I.

Viscometer No. 3967. *Temperature* 70° *F.*

Oil.	Observed Redwood seconds.	ν (cs.) kinematic viscosity.	$\frac{1}{T^2} \times 10^3$.	$\frac{\nu}{T}$.	Calc. $\frac{\nu}{T}$.	$\frac{\text{Calc.-exp.}}{\text{Calc.}}$ per cent.
A	41·75	5·924	0·5737	0·1419	0·1417	−0·14
B	52·4	9·588	0·3642	0·1830	0·1837	+0·38
C	70·9	15·42	0·1990	0·2175	0·2169	−0·28
D	73·5	16·11	0·1851	0·2192	0·2194	+0·09
E	106·65	25·13	0·0879	0·2356	0·2358	+0·08
F	299·1	72·95	0·0112	0·2439	0·2445	+0·25
G	336·4	82·43	0·0088	0·2451	0·2450	−0·04
H	423·5	103·8	0·0056	0·2451	0·2450	−0·04
					Av.	= ±0·17

TABLE II.

Viscometer No. 3967. *Temperature* 140° *F.*

Oil.	Observed Redwood seconds.	ν (cs.) kinematic viscosity.	$\frac{1}{T^2} \times 10^3$.	$\frac{\nu}{T}$.	Calc. $\frac{\nu}{T}$.	$\frac{\text{Calc.-exp.}}{\text{Calc.}}$ per cent.
875P	39·8	4·94	0·6313	0·1241	0·1239	−0·16
ZP	55·5	10·42	0·3247	0·1877	0·1892	+0·79
ES1	77·0	17·04	0·1686	0·2213	0·2210	−0·13
BE	105·8	24·90	0·0893	0·2354	0·2340	−0·60
SGE	145·7	34·91 34·91	0·0471	0·2395	0·2392	−0·13
E30	175·7	42·65 *	0·0324	0·2428	0·2406	−0·91
E40	209·4	50·49	0·0228	0·2412	0·2413	+0·04
E50	268·0	64·86	0·0139	0·2420	0·2419	−0·04
ER	338·4	82·19	0·0087	0·2429	0·2422	−0·29
S120	458·6	110·9	0·0048	0·2417	0·2424	+0·29
S140	558·5	135·7	0·0032	0·2430	0·2425	−0·21
S140A	561·3	135·5	0·0032	0·2414	0·2425	+0·45
HCT2	973·3	236·3	0·0011	0·2429	0·2425	−0·17
					Av.	= ±0·32

* Mean of 42·59 and 42·71.

5·92 to 103·8 centistokes or 41·7 to 423·5 Redwood No. I seconds were investigated.* The experimental results are given in Tables I, II and III,

* Results at 70° F. were limited, since it was known that this temperature was being investigated by Barr.

and it is to be noted that in each case the recorded Redwood times are particular to the viscometer No. 3967, *i.e.* no corrections to "Standard Seconds" have been applied.

TABLE III.

Viscometer No. 3967. *Temperature* 200° *F.*

Oil.	Observed Redwood seconds.	ν (cs.) kinematic viscosity.	$\frac{1}{T^2} \times 10^3$.	$\frac{\nu}{T}$.	Calc. $\frac{\nu}{T}$.	Calc.-exp. / Calc. per cent.
ZP	38·5	4·40	0·6747	0·1143	0·1127	−1·42
LMS	42·3	5·79	0·5589	0·1369	0·1361	−0·59
ESI	44·9	6·71	0·4960	0·1495	0·1499	+0·27
BE	50·7	8·76	0·3890	0·1728	0·1736	+0·46
SGE	59·25	11·63	0·2848	0·1963	0·1965	+0·10
E40	73·2	15·87	0·1866	0·2169	0·2162	−0·32
E50	86·2	19·52* / 19·52	0·1346	0·2264	0·2252	−0·53
ER	101·8	23·58	0·0965	0·2317	0·2309	−0·35
FBF	102·6	23·70	0·0950	0·2310	0·2311	+0·04
S120	127·8	30·32	0·0612	0·2372	0·2352	−0·85
S140	149·35	35·59	0·0448	0·2382	0·2368	−0·59
S140A	149·9	35·60	0·0445	0·2374	0·2368	−0·25
HCT2	214·6	51·08	0·0217	0·2381	0·2386	+0·21
ELL	348·1	82·94† / 83·22 (83·08)	0·0083	0·2386	0·2392	+0·25
					Av.	= ±0·44

* Water-bath.
† Upward flow viscometer.

DISCUSSION OF RESULTS.

When the data in Tables I, II and III are plotted in the manner originally suggested by Higgins,[4] it is apparent that a single straight line will not adequately represent the results at any temperature. This has already been noted for a Redwood No. I viscometer at 70° F. (cf. Garner and Kelly, *loc. cit.*, and Goode and Heath [5]), and it has been suggested that the shape of the Higgins diagram could be covered by the use of two straight-line equations, each applicable to a certain range of outflow times. Such a procedure will give a correlation which may be sufficiently exact for most purposes, but will, however, be an approximation and probably accurate to only ± 1 per cent.

The use of an equation of the type

$$\nu = \frac{T}{10} \times k^{\left(1 - \frac{A}{T^n}\right)}$$

for correlating results obtained on a Saybolt Universal viscometer has already been suggested,[6] whilst a very similar equation has been proposed for correlating Engler degrees and kinematic viscosity by Vogel.[7] It can be shown that such an equation can adequately cover the experimental determinations recorded in this paper, as follows.

When T is large, the value of T^n becomes very large, and hence $\frac{A}{T^n}$ very small.

The equation then condenses to $\nu = \frac{T}{10} \times k$, which becomes applicable when T is greater than 300 seconds approx.

From results at long times of outflow, the value of k can therefore be determined (cf. *e.g.* determinations on oils ER, S120, S140, S140A and HCT2, Table II). Referring to the original equation, this may be written

$$\log \nu = \log T - 1 + \left(1 - \frac{A}{T^n}\right) \log k$$

i.e.

$$1 + \log \nu = \log T + \log k - \frac{A}{T^n} \log k$$

i.e.

$$\frac{A}{T^n} = \frac{\log T + \log k - 1 - \log \nu}{\log k} = y \text{ (say)}.$$

Since the value of k is known, for any pair of values of T and ν, the value of y can be calculated.

Hence

$$A = yT^n$$

or

$$\log A = \log y + n \log T.$$

In other words, by plotting $\log y$ against $\log T$ there should be obtained a straight line from the equation of which the values of A and n can be ascertained. This procedure has been applied to the results in Tables I, II and III, and the following equations have been derived for viscometer No. 3967 at the various test temperatures.

At 70° F. $$\nu \text{ (cs.)} = \frac{T}{10} \times 2{\cdot}45^{\left(1 - \frac{24{,}660}{T^{3{\cdot}443}}\right)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At 140° F. $$\nu \text{ ,, } = \frac{T}{10} \times 2{\cdot}425^{\left(1 - \frac{47{,}800}{T^3}\right)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At 200° F. $$\nu \text{ ,, } = \frac{T}{10} \times 2{\cdot}395^{\left(1 - \frac{75{,}250}{T^{3{\cdot}116}}\right)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Reference to the tables will show the average degree of correlation attained with these equations and the experimental results to be $\pm$ 0·17 per cent. at 70° F., $\pm$ 0·32 per cent. at 140° F. and $\pm$ 0·44 per cent. at 200° F. In view of the increasing experimental difficulties at higher temperatures, particularly with the Redwood No. I viscometer, such concordance is very satisfactory, since only one determination out of the total of thirty-five is outside the probable limit of experimental error, and that is the oil ZP at 200° F., which had a Redwood No. I time of flow of only 38·5 seconds. It would therefore appear that this type of equation is generally applicable to all short-tube efflux viscometers with a small ratio of length to diameter, *e.g.*, 10 or under, for the actual efflux tube.

The equations are useful in that they still apply at extremely low values of the time of outflow, where the kinetic energy correction may amount to over 60 per cent.

From Schiller's [8] work it follows that, for parabolic distribution of velocity during the flow of a liquid through a tube, the ratio $\frac{l}{dR}$ must be

greater than 0·029, where l = tube length, d = tube diameter and R = Reynolds No. The equations appear to hold very accurately down to this point, which for viscometer No. 3967 is reached when the time of flow is about 40 seconds; however, the equations can be used down to lower times of flow, and evidence exists for believing that at 70° F., such an equation is sufficiently accurate for most purposes down to a time of flow of about 30 seconds.

It has not been possible to interpret the shape of the Higgins diagram in a physical sense at the present time. If Schiller's criterion be taken as satisfactorily explaining the lower end of the curve, *i.e.*, say, below 40 seconds, then some effect is occurring around the region where the outflow time is 100 seconds—which at present awaits an explanation. Some experimental work, undertaken to solve this point, is in progress.

Standard Redwood Equations.

(1) *At 70° F.* In order to translate the results obtained on viscometer No. 3967 to standard seconds, *i.e.* those which would be given by viscometer No. 1307, the master viscometer with which all viscometers are compared during comparative flow tests conducted by the National Physical Laboratory,[9] a comprehensive comparison of No. 3967 and No. 1307 was made by Dr. Barr of the N.P.L. The following approximate flow times were selected, as sufficient to define the inter-relationship of these two instruments at all viscosities, viz. 40, 50, 70, 105, 350 seconds, at 70° F.

With this data it was possible to transform equation (1) directly into an equation which represented the kinematic viscosity and Redwood outflow time relationship of viscometer No. 1307.

The equation so obtained was,

$$\nu\,(\text{cs.}) = \frac{T}{10} \times 2{\cdot}47^{\left(1 - \frac{39{,}720}{T^{2{\cdot}415}}\right)} \quad . \quad . \quad (4) \text{ Standard Redwood seconds at } 70° \text{ F.}$$

This equation will reproduce the actual experimental results obtained by Barr,[10] over the range 39·6–994·6 seconds on viscometer No. 1307, with an average error of $\pm$ 0·42 per cent., and moreover if used to calculate the value of the kinematic viscosity corresponding to a flow time of 29·6 seconds, will give a result only 2·5 per cent. in error. The applicability of equation (4) may be tested in another way, as follows. If it be assumed that equation (4) represents the correlation for viscometer No. 1307 and equation (1) the correlation for viscometer No. 3967, then the correction to be applied to viscometer No. 3967 for any flow time may be calculated. In Table IV are shown the calculated corrections for viscometer No. 3967 and the corrections actually obtained by the National Physical Laboratory.

Table IV.

Redwood time at 70° F. Viscometer No. 3967, secs.	Calculated correction to give standard seconds, secs.	Correction as determined by N.P.L., secs.
41·75	−1·50	−1·45
52·4	−1·75	−1·9
73·5	−2·0	−2·0
106·0	−1·75	−1·8
336·4	−2·7	−2·3

Finally, the results given by equation (4) are in good agreement with the two approximate equations in the recent 1935 edition of the "Standard Methods for Testing Petroleum and Its Products."

(2) *At* 140° *F. and* 200° *F.* In order to transform equations (2) and (3) into expressions dealing with standard seconds, it was necessary to assume that the relationship between viscometers Nos. 1307 and 3967, determined at 70° F., applied also at these higher temperatures. The assumption was partly tested in the following manner. Two viscometers which were known to give identical results at 70° F. were carefully compared at 140° F. and 200° F. It was found that at the higher temperatures the same relation existed. Both these instruments were of relatively recent construction, so that it does not follow automatically that instruments 1307 and 3967 will necessarily have the same relationship at the temperatures of 70° F., 140° F. and 200° F., but failing direct comparison, the assumption cannot be tested in any other way. At the same time, the data on which equations (2) and (3) are based were obtained with the receiving flask insulated, so that it was necessary to obtain comparative data with the flasks uninsulated. It was found that at 140° F. the effect of insulation was negligible, as it was well within the limits of experimental error. Results obtained at 200° F. were such that the times of flow with uninsulated flasks were, on the average, 0·25 per cent. longer than when the flasks were insulated. The application of this correction appeared to be justified.

For standard seconds at 140° F. the following equation was thus deduced.

$$\nu\,(\text{cs.}) = \frac{T}{10} \times 2{\cdot}45^{\left(1-\frac{81{,}190}{T^{2\cdot 188}}\right)} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Similarly for standard seconds at 200° F. the following equation was derived :—

$$\nu\,(\text{cs.}) = \frac{T}{10} \times 2{\cdot}415^{\left(1-\frac{97{,}950}{T^{2\cdot 3885}}\right)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In connection with equation (6) it must be noted that it is applicable only over the range of viscosities investigated, *i.e.* it must be used only up to 350 seconds. Even so, results calculated for times in excess of 200 seconds may be 0·50 per cent. high, and it is suggested therefore that for times of flow of 200–400 seconds at 200° F. the simple equation

$$\nu\,(\text{cs.}) = 0{\cdot}2400T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

be used.

The reason for the fall of values of $\frac{\nu}{T}$ at long times of flow at 200° F. may be attributed to the facts considered in the introduction of this paper, *i.e.* cooling of the jet and cooling of the oil in the receiving vessel.

In this connection, the true physical significance of the type equation used to correlate the results, will hold only at 70° F. The equations derived for 140° F. and 200° F. represent mathematical adjustments to take care of the various cooling factors,—for example, that due to the jet temperature being lower than the nominal temperature of test. It seems possible that the jet temperature varies with actual oil viscosity, but it is believed

that equations (4), (5) and (6) represent the correlations between Redwood seconds at 70° F., 140° F. and 200° F. and kinematic viscosity in centistokes to within $\pm 0{\cdot}50$ per cent.

In order to render the correlation more easily applicable, Table V has

TABLE V.

Conversion Table for Redwood Seconds and Kinematic Viscosity.

Kinematic Viscosity, Centistokes.	Redwood No. I seconds at			
	70° F.	*	140° F.	200° F.
4·0	35·3	—	35·95	36·3
5·0	37·9	—	38·45	38·9
6·0	40·5	40·5	41·05	41·5
7·0	43·2	43·2	43·7	44·15
8·0	46·0	46·0	46·35	46·9
9·0	48·85	48·85	49·1	49·65
10·0	51·7	51·8	52·0	52·55
11·0	54·75	54·75	55·0	55·6
12·0	57·9	57·9	58·1	58·75
13·0	61·05	61·05	61·3	61·95
14·0	64·35	64·25	64·55	65·25
15·0	67·7	67·5	67·95	68·75
16·0	71·15	70·8	71·4	72·2
17·0	74·65	74·1	74·85	75·75
18·0	78·1	77·5	78·45	79·35
19·0	81·7	80·9	82·1	83·1
20·0	85·4	84·3	85·75	86·9
21·0	89·2	88·0	89·5	90·7
22·0	92·9	91·9	93·25	94·5
23·0	96·7	95·8	97·05	98·3
24·0	100·4	99·8	100·9	102·2
25·0	104·2	103·8	104·7	106·1
26·0	108·1	107·7	108·6	110·0
27·0	111·9	111·7	112·5	114·0
28·0	115·8	115·6	116·5	118·0
29·0	119·7	119·7	120·4	122·0
30·0	123·7	123·6	124·4	126·0
32·0	131·5	131·6	132·3	134·1
34·0	139·3	139·5	140·2	142·2
36·0	147·2	147·5	148·2	150·3
38·0	155·2	155·5	156·2	158·3
40·0	163·2	163·6	164·3	166·7
42·0	171·2	171·6	172·3	175·0
44·0	179·2	179·6	180·4	183·3
46·0	187·2	187·6	188·5	191·7
48·0	195·3	195·7	196·6	200·0
50·0	203·3	203·7	204·7	—
55·0	223·4	223·9	225·0	—
60·0	243·5	244·0	245·3	—
65·0	263·6	264·1	265·7	—
70·0	283·9	284·3	286·0	—
75·0	304·0	304·5	306·3	—

* Values calculated by official I.P.T. equations. (See "Standard Methods," Third Edition, 1935).

At 70° F. $T = 4{\cdot}049 \times \nu$ for times above 300 seconds.
At 140° F. $T = 4{\cdot}082 \times \nu$, " " " " "
At 200° F. $T = 4{\cdot}167 \times \nu$, " " of 200–400 seconds.
where T = Redwood No. I seconds.
and ν = Kinematic viscosity in centistokes.

been prepared, which will serve as a skeleton conversion table from which appropriate graphs can be constructed. The Redwood times quoted at 70° F. will diverge a little from those calculated by the simple equations given in Serial Designation L.O. 8 ("Standard Methods for Testing Petroleum and its Products," I.P.T. 3rd Edition, 1935), since the latter is admittedly only accurate to $\pm$ 1·0 per cent.

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I.P.T. VISCOSITY CONVERSION TABLE FOR CENTISTOKES AND REDWOOD SECONDS AT 70° F., 140° F., AND 200° F.

By the Viscosity Panel of the I.P.T. Standardization Committee.

In 1934 the Viscosity Panel of the Institution of Petroleum Technologists arranged a programme of work to revise the formula for converting

I.P.T. Viscosity Conversion Table for Centistokes and Redwood Seconds.

Centistokes.	Redwood Seconds at			Centistokes.	Redwood Seconds at		
	70° F.	140° F.	200° F.		70° F.	140° F.	200° F.
4	35·3	35·95	36·3	41·0	167·0	168·3	170·8
4·5	36·55	37·2	37·6	42·0	171·0	172·3	175·0
5·0	37·9	38·45	38·9	43·0	175·1	176·4	179·2
5·5	39·2	39·8	40·15	44·0	179·1	180·4	183·3
6·0	40·5	41·05	41·5	45·0	183·1	184·5	187·5
6·5	41·85	42·4	42·8	46·0	187·1	188·5	191·7
7·0	43·2	43·7	44·15	47·0	191·2	192·6	195·8
7·5	44·55	45·0	45·5	48·0	195·2	196·6	200·0
8·0	46·0	46·35	46·9	49·0	199·2	200·7	204·2
8·5	47·4	47·75	48·25	50·0	203·3	204·7	208·3
9·0	48·85	49·1	49·65				
9·5	50·25	50·55	51·1	60·0	243·5	245·3	250·0
10·0	51·7	52·0	52·55	70·0	283·9	286·0	291·7
				80·0	324	327	333
11·0	54·75	55·0	55·6	90	364	367	375
12·0	57·9	58·1	58·75	100	405	408	417
13·0	61·05	61·3	61·95				
14·0	64·35	64·55	65·25	110	445	449	—
15·0	67·7	67·95	68·75	120	486	490	—
16·0	71·0	71·4	72·2	130	526	531	—
17·0	74·4	74·85	75·75	140	567	571	—
18·0	77·9	78·45	79·35	150	607	612	—
19·0	81·4	82·1	83·1	160	648	653	—
20·0	85·0	85·75	86·9	170	688	694	—
				180	729	735	—
21·0	88·7	89·5	90·7	190	769	776	—
22·0	92·4	93·25	94·5	200	810	816	—
23·0	96·1	97·05	98·3				
24·0	99·9	100·9	102·2	210	850	857	—
25·0	103·7	104·7	106·1	220	891	898	—
26·0	107·5	108·6	110·0	230	931	939	—
27·0	111·4	112·5	114·0	240	972	980	—
28·0	115·3	116·5	118·0	250	1012	1021	—
29·0	119·2	120·4	122·0	260	1053	—	—
30·0	123·1	124·4	126·0	270	1093	—	—
				280	1134	—	—
31·0	127·0	128·3	130·1	290	1174	—	—
32·0	131·0	132·3	134·1	300	1215	—	—
33·0	134·9	136·3	138·1				
34·0	138·9	140·2	142·2	310	1255	—	—
35·0	142·9	144·2	146·2	320	1296	—	—
36·0	146·9	148·2	150·3	330	1336	—	—
37·0	150·9	152·2	154·2	340	1377	—	—
38·0	155·0	156·2	158·3	350	1417	—	—
39·0	159·0	160·3	162·5				
40·0	163·0	164·3	166·7				

For Redwood times above 1400 seconds at 70° F., Redwood seconds = 4·05 × cs.
Accuracy of table plus or minus 0·5%.

Redwood I seconds to kinematic viscosities, which was first prepared by Higgins in 1913. The results of this investigation at the National Physical Laboratory are given in a paper by Barr,[1] who confined his work to 70° F. It has been found that three different conversion factors are necessary to express the relationship at the three standard temperatures of 70° F., 140° F. and 200° F.[2]

In the table are given the authoritative equivalents in Redwood I seconds at 70° F., 140° F. and 200° F. of kinematic viscosities in centistokes. The formulæ given by Barr and by Garner, Broom and Taylor, for 70° F. lead to almost identical results, except in the range 15 to 42 cs. Mean values have been tabulated for this interval, which in no case differ by as much as 0·5 per cent. from those calculated by either formula.

The I.P.T. Viscosity Nomogram,* which is based on the figures given in the table, consists of five lines for the conversion of Redwood I seconds at 70° F. to centistokes over the range of 35–3250 seconds, which covers the viscosity range likely to be used in practice. It will be noticed that the scales on the individual lines overlap, and this has been arranged for convenience in use. For higher viscosities than 3250 centistokes any of the last three lines can be used by multiplying by 10. For example, the centistokes reading of 3500 Redwood I seconds is 862. For Redwood I seconds at 140° F., four lines are given covering the useful working range, and similarly for Redwood I seconds at 200° F. three lines are given.

References.

[1] Barr, G., "The Relation between Redwood Seconds and Kinematic Viscosities," *J.I.P.T.*, 1936, **22**, 1–10.

[2] Garner, F. H., Broom, W. E. J., and Taylor, J. L., "Redwood-Kinematic Relationships at 70° F., 140° F. and 200° F.," *J.I.P.T.*, 1936, **22**, 11–20.

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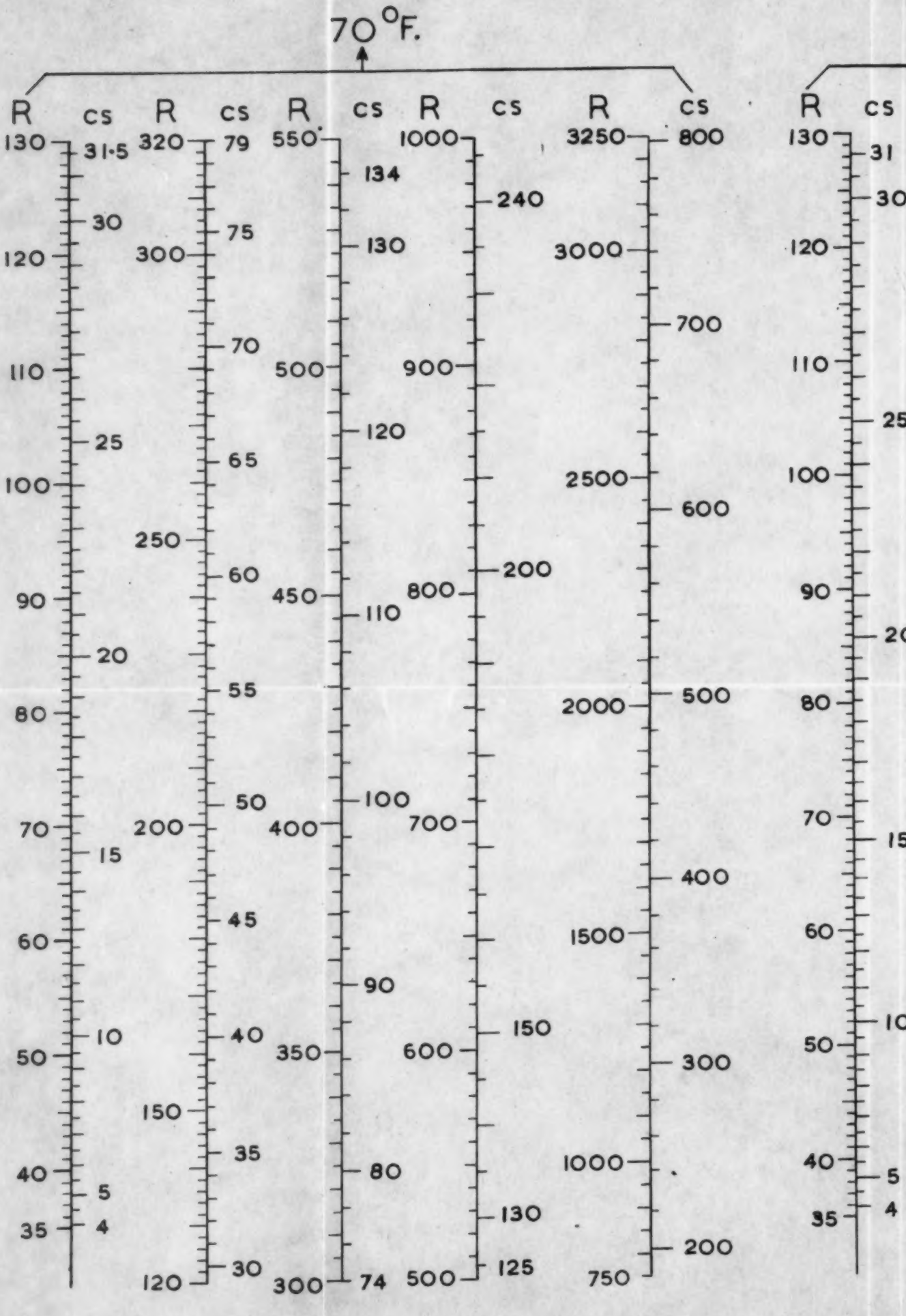
* Reproductions of the Nomogram and the complete paper, printed on card, can be obtained from the Institution of Petroleum Technologists, Aldine House, Bedford Street, London, W.C. 2, price 2*s.* 6*d.* post free.

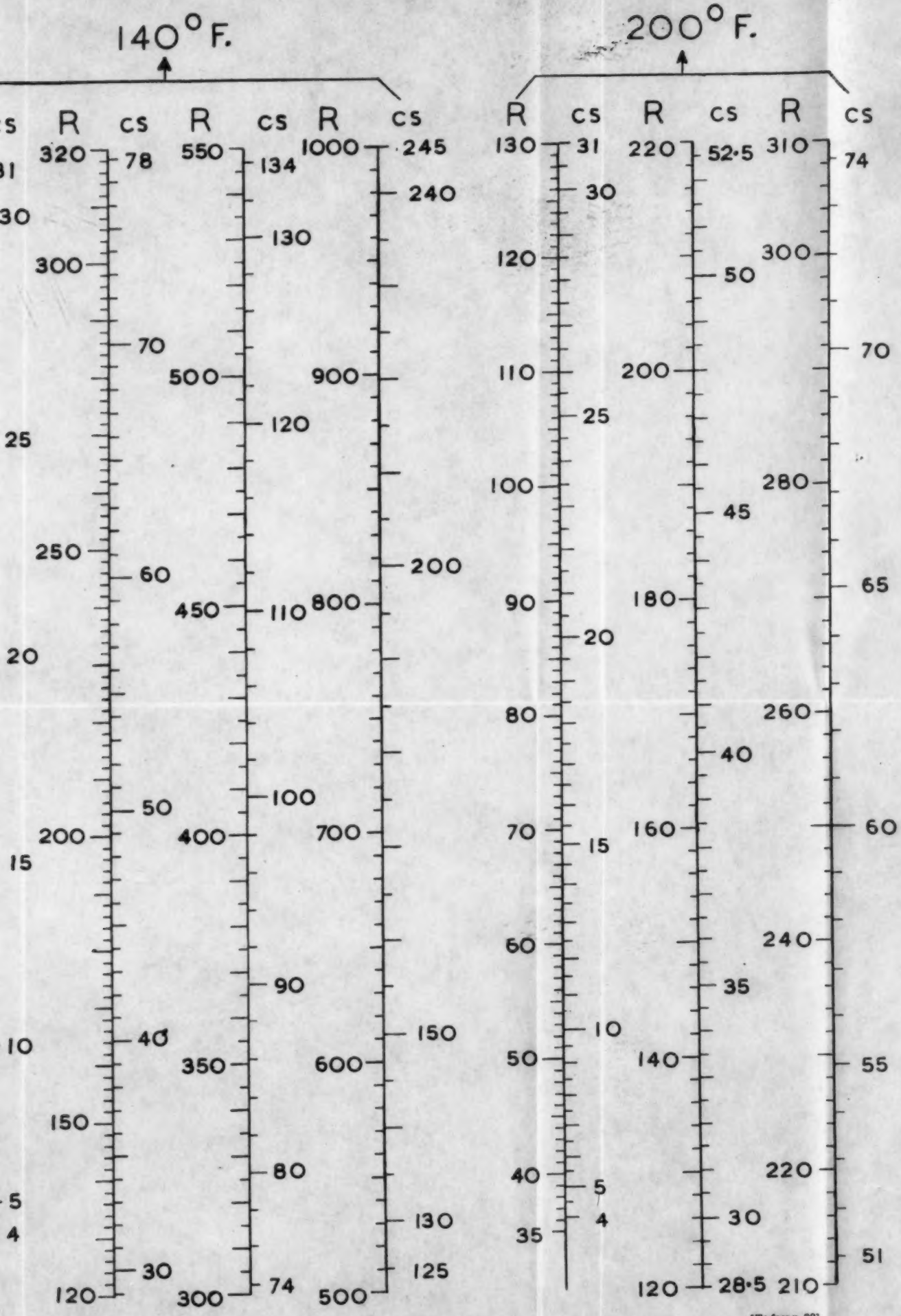
I.P.T. VISCOSITY

REDWOOD No.1 SECONDS (F



Y NOMOGRAM

(R) AND CENTISTOKES (cs)



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DRAINAGE ERRORS AND U-TUBE VISCOMETERS.

By W. E. J. Broom, B.Sc., Ph.D. (Associate Member).

The problem of drainage in relative viscometers of the U-tube or Ostwald type has furnished grounds for some speculation, but little accurate data have been available. In general, it has often been assumed that, with well-designed viscometers, errors due to drainage were negligible. This assumption would appear to be approximately correct, and it is the purpose of this note to review some published data by Cannon and Fenske [1] which may help to stimulate thought on this problem.

Errors due to incomplete drainage in U-tube viscometers would appear to fall into two categories. First, when the liquid under examination is aspirated from the lower to the upper bulb, the effect is to cause an increased initial head, thus tending to cause a decreased time of flow. In normal usage, this movement of the liquid under examination will be the most rapid one which it will undergo, and such movement will not be effected under any given set of constant conditions. The error will be minimized by aspirating slowly and by correct design of the lower bulb, which should be of ample proportions, particularly in regard to diameter.

The second type of error will be that caused by the retention of a film of liquid on the walls of the timing bulb. This may be regarded as reducing the volume which is timed between the marks on the timing bulb. The effect will be to reduce the time of flow. It is this second type of error which will be considered here.

The volume of the retained film of liquid on the timing bulb would be expected to be related to the following factors :

(*a*) Surface tension of liquid, γ,
(*b*) Surface area, S, of timing bulb,
(*c*) Viscosity of liquid, ν, in centistokes,
(*d*) Time of flow of liquid between timing marks, t.

The relative percentage error, E, may thus be expressed

$$E \propto \phi(S/V)\phi'(\nu)\phi''(t)\phi''(\gamma)$$

where V = volume of timing bulb.

Confining the discussion to petroleum oils, the effect of surface tension may be omitted, since it varies but little for these products. We may thus write :

$$E = k'\phi(S/V)\nu^x t^{-y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for any given viscometer

$$E = \frac{k\nu^x}{t^y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

since S and V are constant.

The above expression may be simplified further, since for U-tube viscometers, $\nu = \text{const.} \times t, = a \times t$,

hence

$$E = \frac{k \times a^x \times t^x}{t^y} = ka^x t^y = Kt^y \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If it be assumed that $x = y$ in equation (3), then E = constant. In other words, calibration with a petroleum oil would ensure correct results for future determinations on petroleum oils in so far as drainage is concerned.

The above considerations will now be applied to data given by Cannon and Fenske (*loc. cit.*), which are given in Table I. It is to be noted that these authors state that the only dimension which differed in the two viscometers was that of the capillary diameter, and hence the surface/volume relationship and actual volume of the timing bulbs were, no doubt, as nearly similar as could be realized in manufacture. The error recorded in Table I was obtained as follows. A weighed bulb, similar in shape to

TABLE I.

Oil.	Observed Time (secs.).	Drainage Correction (per cent.).	Kinematic (centistokes at 100° F.).
Small-bore Master Viscometer. Constant = 27,100 sec./stokes = 0·00369 cs./secs.			
1G	581·4	+ 0·05	2·145
2G	2,355	+ 0·08	8·690
3G	5,661	+ 0·10	20·91
4G	11,955	+ 0·13	44·17
Large-bore Master Viscometer. Constant = 1056 sec./stokes = 0·09469 cs./secs.			
3G	220·5	+ 0·15	20·90
4G	465·0	+ 0·30	44·15
5G	887·8	+ 0·24	84·23
6G	1,841	+ 0·28	174·7
7G	3,296	+ 0·34	313·2
8G	7,808	+ 0·36	741·1
9G	12,607	+ 0·35	1198

that of the viscometer timing bulb, but with no capillary attached, was filled with the oil under test, and then allowed to empty and drain, for a time equal to that recorded in the "observed time" column, at a temperature of 100° F. The weight of oil adhering was then obtained, from which the necessary correction could be calculated. This procedure assumes that the volume retained on the walls of the bulb will be the same for a given total time of drainage irrespective of the rate of fall of the oil level, which, while not correct, can probably be admitted as a first approximation, when allowance is made for the actual magnitude of drainage errors.

The data in Table I are shown graphically in Fig. 1, and while the data for the small-bore viscometer lie along a smooth curve which indicates increasing error with increasing outflow time, *i.e.* increasing viscosity, the data for the large-bore viscometer indicate, first, that the point for oil 4G is probably inaccurate, and secondly that an apparent constant degree of error is attained when the viscosity exceeds a value corresponding to an outflow time of about 6000 seconds.

Considering the two results with oil 3G, where the viscosity is, of course, constant, the dependence of the drainage error on time of outflow may be calculated, since

$$\frac{0{\cdot}15}{0{\cdot}10} = \frac{220{\cdot}5^{y}}{5661^{y}}$$

from which $$y = -0{\cdot}125$$

Hence, for constant S/V and constant viscosity, $E = kt^{-0{\cdot}125}$.

We may now insert the above value of y into equation (2) and apply this equation to the results for oils 1G and 4G in the small viscometer, viz. $E = 0{\cdot}05$, $t = 581{\cdot}4$ and $E = 0{\cdot}13$, $t = 11{,}955$, we find $x = 0{\cdot}441$. Hence

$$E = k \cdot \frac{\nu^{0{\cdot}441}}{t^{0{\cdot}125}} = \frac{k \,.\, a \,.^{0{\cdot}441} t^{0{\cdot}441}}{t^{0{\cdot}125}}$$

Equation (3) then becomes

$$E = K \,.\, t \,.^{0{\cdot}316}$$

The applicability of this equation to the runs on the small-bore viscometer is shown in Table II, since the quantity $E/t^{0{\cdot}316}$ should be constant. The

TABLE II.

Small-bore Viscometer.

Oil.	Value of $E/t^{0{\cdot}316}$.
1G	$6{\cdot}69 \times 10^{-3}$
2G	$6{\cdot}89 \times 10^{-3}$
3G	$6{\cdot}52 \times 10^{-3}$
4G	$6{\cdot}68 \times 10^{-3}$

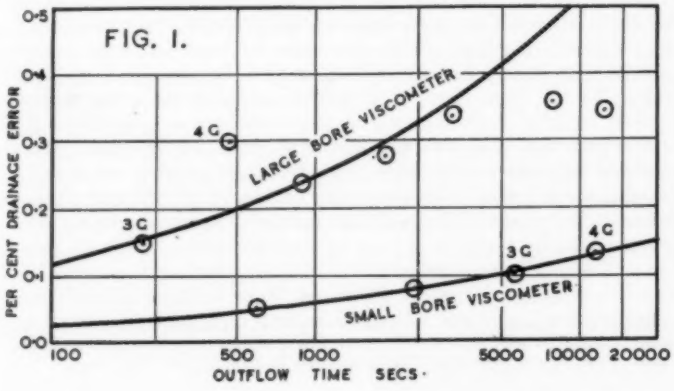
Mean value $= 6{\cdot}70 \times 10^{-3}$.

mean value of K is $6{\cdot}70 \times 10^{-3}$ and this equals, cf. equation (3), $k \times a^{0{\cdot}441}$, where k is the surface/volume constant and a the viscometer constant. The value of K' for the large-bore viscometer should therefore be equal to :

$$K \times \left(\frac{0{\cdot}09469}{0{\cdot}00369}\right)^{0{\cdot}441} = 2{\cdot}802 \times 10^{-2}$$

The drainage error of the large-bore viscometer should therefore be given by

$$E = 2{\cdot}802 \times 10^{-2} \times t^{0{\cdot}316}$$



The curve in Fig. 1 for the results on the large-bore viscometer has been calculated from this equation, and fits the data well up to 3000 seconds. It should be emphasized that the above derivation is based on the two values of error obtained with oil 3G, since it appears that one result on oil 4G is incorrect. Thus the departure of the points from the calculated line when t exceeds 3000 seconds may be due to experimental error, to an inadequacy of the method of analysis, or to the possibility that the surface volume relationship of the timing bulb of the large-bore viscometer was not as nearly equal to that of the small-bore viscometer as demanded by the theory.

Since in practice a particular U-tube viscometer is generally constructed to give accurate results above 100 seconds, and is used for oils the times of flow of which in the instrument do not exceed 1000 seconds,[2] the simple form of equation expressing the drainage error would certainly seem adequate over this range.

It is also possible to make some interesting deductions from the drainage equation, $E = k \,.\, a^{0\cdot441} t^{0\cdot316}$, which should be general to all viscometers, where k will depend largely on the configuration and volume of the timing bulb and a will be the instrument constant. For example, the drainage error in a given viscometer will increase with increasing time of flow, but such an increase is proportional only to $t^{0\cdot316}$, which indicates that at 1000 seconds time of flow the error will be about twice the error at 100 seconds. Suitable choice of dimensions and calibration with an oil of 500 seconds time of flow can thus easily ensure that relative drainage errors are negligible.

Further, the relatively small effect of increased viscosity (*i.e.* increased time of flow) will mean that, in any series of viscometers where the ratio S/V is substantially constant and capillary diameter is the only important variable, the absolute error due to drainage will increase as the capillary diameter increases, or, in other words, as the viscometer constant increases. The two sets of results in Fig. 1 illustrate this point, *e.g.* oil 3G. In order to preserve the same absolute error throughout a series of viscometers, it is therefore necessary to decrease the ratio S/V as the viscometer constant, expressed in cs./secs., increases, but it would be expected that this ratio could not conveniently be decreased to the necessary degree to render the drainage error constant, and therefore that the absolute error would increase with increase in the value of the viscometer constant. Finally, it will clearly be advisable to make the ratio S/V as small as possible. To this end, Barr [3] has indicated a good shape for the timing bulb.

It is hoped that this note will stimulate work on the accurate determination of drainage error, which might easily be carried out using bulbs fitted with ground-glass joints to carry capillaries of different diameters. In this way, the retained film could be estimated under conditions identical with those actually found in the use of the viscometer.

References.

[1] Cannon and Fenske, *Oil & Gas Journal*, April 11th, 1935, p. 52.
[2] Compare *B.S.S.* 188, 1929. "Determination of Viscosity in Absolute Units."
[3] Barr, *Proc. World Petroleum Congress*, 1933, 2, 508.

ACCURACY OF ENGLER VISCOSITIES.*

By F. H. Garner, Ph.D., M.Sc., F.I.C. (Member), and W. E. J. Broom, B.Sc., Ph.D. (Associate Member).

Introduction.

At the present time, particularly where the viscosity–temperature relationships of lubricating oils are concerned, there is a demand from the commercial point of view for the determination of viscosity to a higher degree of accuracy than can readily be obtained with the Engler viscometer.

This mainly applies in connection with the use of Viscosity Index, which is being so widely adopted not only in the United States, but also in various countries in Europe, as a method for the expression of the viscosity–temperature characteristics of oils.

Until such time arrives that kinematic (or absolute) viscosity is universally recognized and used to express the viscosity of petroleum products, efforts must be made to establish accurate measurement by the commercial viscometers in use to-day and accurate interconversion formulæ, so that kinematic viscosity may be readily derived from the more conventional units now in use.

Even when Engler instruments have been checked for dimensions and water equivalent by the Physikalisch-Technischen Reichsanstalt at Charlottenburg, there is no guarantee that concordant results will be obtained with different instruments, and, in fact, such procedure as is adopted at the present time is not sufficient to ensure uniformity.

It would appear necessary to adopt comparative flow tests with one or more oils, against a standard viscometer, as is done with the Saybolt and Redwood viscometers, in order to increase the precision of the measurements.

The oils selected would cover the normal working range of the viscometer, and so a comparison could be effected under more reproducible conditions than those at present found when a comparison is made with a liquid (*i.e.* water) of markedly different surface tension, and moreover with so low a viscosity that the observed outflow time requires a correction of approximately 87 per cent., due to kinetic energy effects, in order to obtain a time directly proportional to viscosity.

It is interesting to note that it is now a commonly adopted practice to determine viscosity in an apparatus giving kinematic viscosity direct, *e.g.* Vogel–Ossag or Baume–Vigneron, and to calculate the Engler viscosity by means of a conversion formula since, by this means, more accurate agreement is obtained between one laboratory and another, than by actually determining the Engler viscosity.

The purpose of the present paper is to indicate results which have been obtained by a group of laboratories situated in various countries in Europe, under carefully-controlled conditions, using in most cases instruments

* Paper received November 5th, 1935.

which have been calibrated at Charlottenburg. These results show a very wide range—much greater than would be obtained with such instruments as the Redwood and Saybolt viscometers—and it is felt that these differences are largely due to the fact that the Engler instrument is calibrated with water, of which the viscosity is so low that it is actually right outside the working limits of the instrument.

Reproducibility of Results with the Engler Viscometer.

Experience with the Engler viscometer indicates that results are often obtained which do not check well with viscosities reported by other laboratories on the same samples of oil. This experience parallels that of Wieck,[1] who noted that two Engler viscometers which both passed the dimensional requirements and limits on the water rate at 20° C., failed to give concordant results when used to determine oil viscosities. Differences amounting to 4·8 per cent. were, in fact, observed.

With the object of investigating the degree of concordance to be expected between two Engler viscometers when operated in different laboratories, and at the same time to obtain data which would assist in developing an accurate interconversion of the results given by the common viscometers in use in various countries, ten oils were circulated amongst eight oil laboratories in Germany, France, Holland, Denmark, United States of America, and England.

The results reported are listed in Table I, and it is to be noted that where one laboratory has reported two results, these represent two different Engler viscometers.

It is apparent that good agreement is not obtained, *e.g.* oil No. 7 at 50° C. is reported as having viscosities varying from 10·03 to 11·03°, and it was decided to treat the results statistically. The mean Engler viscosities were therefore calculated and taken as correct, and at the same time the standard error of the mean value, *i.e.* the S.E.M., was derived. This latter equals $\pm \frac{\sigma}{\sqrt{n}}$, where n is the number of separate values reported for each oil and σ is the standard deviation. The latter equals $\pm \sqrt{\frac{\Sigma v^2}{n}}$, where Σv^2 is the summation of the squares of the deviations from the mean value for the reported values of a particular determination.

The substantial accuracy of this procedure is indicated by comparing column J with the mean values recorded in Table I. In column J are results obtained by Prof. L. Ubbelohde, which were obtained later, and so furnish a check on the mean values deduced from the other laboratories.

The S.E.M. computed represents the degree of uncertainty to which the mean value is known, whereas the standard deviation is the likely uncertainty in a single reported result. These results are given in Table II.

By plotting the information given in Table II there can be derived Table III, which indicates the likely experimental error in an Engler viscosity as reported by a single laboratory.

In general, the error increases with increasing viscosity and for a given viscosity, with increasing temperature of test. At low viscosities, *i.e.* below 2·0° E., the error is approximately constant at about 2·0 per cent.

TABLE I.

Co-operative Work on Engler Viscometer.

Oil.	Lab. A.		B.		C.	D.	E.	F.	G.	H.	Mean Result.	J.
	(1)	(2)	(1)	(2)								
No. 1 at 25° C. . .	3·78	3·78	3·58	3·70	3·85	3·70	3·66	—	—	—	3·72 ± 0·03	3·78
No. 1 at 50° C. . .	1·94	1·95	1·84	1·89	1·88	1·85	1·93	—	—	—	1·90 ± 0·015	1·90
No. 2 at 25° C. . .	6·10	6·18	5·80	5·97	5·72	5·97	5·90	—	—	—	5·95 ± 0·06	6·00
No. 2 at 50° C. . .	2·42	2·42	2·31	2·36	2·33	2·35	2·38	—	—	—	2·37 ± 0·015	2·39
No. 3 at 25° C. . .	8·08	8·02	7·60	7·91	8·00	7·81	7·61	—	—	—	7·86 ± 0·07	7·97
No. 3 at 50° C. . .	2·90	2·91	2·78	2·87	2·80	2·75	2·94	—	—	—	2·85 ± 0·025	2·86
No. 4 at 25° C. . .	10·71	10·63	10·05	10·37	10·30	10·39	10·10	—	—	—	$10·36_5$ ± 0·085	10·44
No. 4 at 50° C. . .	3·45	3·46	3·28	3·40	3·49	3·30	3·34	—	—	—	3·39 ± 0·03	3·35
No. 4 at 100° C. . .	1·49	1·49	1·43	1·45	1·48	1·42	1·42	—	—	—	$1·45_5$ ± 0·01	1·44
No. 5 at 25° C. . .	14·94	15·24	14·20	14·75	14·27	14·60	14·25	—	—	—	14·61 ± 0·14	14·91
No. 5 at 50° C. . .	4·29	4·24	4·00	4·11	4·20	4·04	4·04	—	—	—	4·13 ± 0·04	4·10
No. 5 at 100° C. . .	1·56	1·51	1·49	1·52	1·54	1·49	1·52	—	—	—	1·52 ± 0·01	1·49
No. 6 at 25° C. . .	35·91	35·84	33·60	34·90	34·20	34·89	33·40	—	—	—	34·68 ± 0·35	35·45
No. 6 at 50° C. . .	7·45	7·39	6·96	7·25	7·33	6·94	7·15	—	—	—	7·21 ± 0·07	7·21
No. 6 at 100° C. . .	1·76	1·76	1·68	1·72	1·74	1·68	1·68	—	—	—	1·72 ± 0·01	1·71
No. 7 at 50° C. . .	10·83	10·72	10·27		11·03	10·10	10·04	10·63	10·03	10·55	10·47 ± 0·12	—
No. 7 at 100° C. . .	$2·23_5$	$2·17_5$	2·12		2·19	2·12	2·10	2·08	2·15	$2·17_5$	2·15 ± 0·015	—
No. 8 at 50° C. . .	18·47	18·25	17·25		18·63	16·64	16·76	—	16·49	17·85	17·54 ± 0·28	—
No. 8 at 100° C. . .	$2·88_5$	$2·89_5$	2·75		2·91	2·75	2·78	—	2·71	2·82	2·81 ± 0·025	—
No. 9 at 50° C. . .	30·25	31·18	29·45		31·16	28·20	28·31	29·81	28·86	30·40	29·74 ± 0·35	—
No. 9 at 100° C. . .	$4·05_5$	$4·07_5$	3·84		4·04	3·87	3·91	3·79	3·86	$3·94_5$	3·93 ± 0·03	—
No. 10 at 50° C. . .	56·26	54·47	55·94		59·10	54·42	52·99	56·59	53·50	57·05	55·59 ± 0·61	—
No. 10 at 100° C. . .	5·58	$5·67_5$	5·34		5·60	5·06	5·36	5·16	5·34	5·42	5·39 ± 0·06	—

TABLE II.

Table of Errors.

Oil.	25° C.			50° C.			100° C.		
	σ. Per cent.	S.E.M. Per cent.	Actual E°.	σ. Per cent.	S.E.M. Per cent.	Actual E°.	σ. Per cent.	S.E.M. Per cent.	Actual E°.
No. 1	2·23	0·83	3·72	2·16	0·82	1·90	—	—	—
No. 2	2·52	0·96	5·95	1·69	0·63	2·37	—	—	—
No. 3	2·29	0·86	7·86	2·46	0·91	2·85	—	—	—
No. 4	2·21	0·83	10·36$_5$	2·27	0·86	3·39	1·99	0·76	1·455
No. 5	2·53	0·96	14·61	2·52	0·94	4·13	1·58	0·59	1·52
No. 6	2·67	1·01	34·68	2·64	1·00	7·21	2·09	0·78	1·72
No. 7	—	—	—	3·35	1·15	10·47	2·14	0·70	2·15
No. 8	—	—	—	4·61	1·60	17·54	2·56	0·89	2·81
No. 9	—	—	—	3·57	1·18	29·74	2·47	0·76	3·93
No. 10	—	—	—	3·27	1·10	55·59	3·53	1·11	5·39

TABLE III.

Experimental Error at Various Test Temperatures.

Engler Viscosity.	25° C. Per cent.	50° C. Per cent.	100° C. Per cent.
1	—	1·8	1·5
2	—	2·1	2·0
3	2·2	2·3	2·5
4	—	2·5	3·0
5	2·3	2·6	3·4
10	2·4	3·0	—
15	2·5	3·2	—
20	2·6	3·4	—
30 and above	2·7	3·5	—

Since this error can be positive or negative from the correct value, it follows that in comparing the results reported by two laboratories, differences of at least 3·0–7·0 per cent. can be expected, depending on the actual viscosity of the oil under test and the temperature at which the determination is conducted.

The unsuitability of the Engler viscometer, as at present in use, for even reasonably accurate work is well demonstrated by these results. The position has doubtless arisen owing to the fact that no standard instrument is available against which all other Engler viscometers can be directly compared in the manner, for instance, that Redwood No. I viscometers are standardized at the National Physical Laboratory, England, or Saybolt instruments at the Bureau of Standards, United States.

Detailed examination of the results obtained by each separate laboratory reveals that the differences obtained from the mean values are, in general, perfectly regular, and can be plotted to yield correction charts, which fact, in turn, indicates that each viscometer gives results which differ in a definite manner from the mean, and that actual comparative flow tests with a standard instrument would largely eliminate the differences found. The

data given in this paper would indicate that such comparative flow tests could be conducted with advantage, at more than one temperature.

Since the kinematic viscosities of oils Nos. 7, 8, 9 and 10 are known from determinations using B.S.I. U-tube viscometers, the applicability of Vogel's equation * connecting kinematic viscosity and Engler degrees can be tested. The results in Table IV show that, apart from two results, the percentage differences between the calculated and observed values of kinematic viscosity (col. 5) are smaller than the uncertainty (col. 6) in the experimental value of the Engler viscosity from which the calculated kinematic viscosity is derived. It is considered, therefore, that Vogel's formula is of sufficient accuracy to correlate satisfactorily kinematic viscosity and Engler degrees.

TABLE IV.

(1) Mean Engler Result.	(2) Test Temp.	(3) Observed.	(4) Calc.	(5) $\frac{(4)-(3)}{(3)}$ as per cent.	(6) S.E.M. Per cent.
2·15	100° C.	13·23	13·32	+0·68	±0·70
2·81	,,	19·29	19·48	+0·99	±0·89
3·93	,,	28·85	28·89	+0·14	±0·76
5·39	,,	40·31	40·43	+0·30	±1·11
10·47	50° C.	79·55	79·41	−0·18	±1·15
17·54	,,	134·1	133·2	−0·67	±1·60
29·74	,,	228·3	226·0	−1·01	±1·18
55·59	,,	429·7	422·5	−1·68	±1·10

It is perhaps significant that the calculated results at 100° C. all differ from the determined kinematic viscosities in a positive direction, whereas the results at 50° C. lie in a negative direction. In view of the figures supplied in Table III, however, any adjustment in Vogel's formula would be quite unjustified at the present time. If, in the future, the Engler viscometer should be standardized against a master viscometer at temperatures of *e.g.* 20° C., 50° C. and 100° C., then, and only then, could such differences as are found in the calculated and kinematic viscosities be taken care of by modifying the simple Vogel equation, perhaps by the inclusion of a temperature factor as suggested by Vogel [2] himself.

References.

[1] Wieck, "Compte-Rendu. Congrès du Graissage," Strasbourg, 1931, p. 206.
[2] Vogel, *Zeit. f. angew. Chem.*, 1922, **35**, 561.

* ν centistokes $= E \times 7{\cdot}6\left(1-\frac{1}{E^3}\right)$.

THE SUSPENDED LEVEL VISCOMETER.*

By Prof. Dr. L. Ubbelohde.

Some capillary viscometers permit the viscosity to be determined so accurately that only a small correction for kinetic energy and surface tension need be applied. For the suspended level viscometer, the necessary corrections are set out below. Short descriptions of the viscometer have already been published.[1]

The Viscometer.

From the pipette bulb A (Fig. 1), with its timing marks m_1 and m_2, the capillary 4 leads to the hollow vessel C, which is about 12 mm. in diameter. The funnel-shaped lower end of the capillary is situated in the middle of the flat face which lies at right angles to the capillary axis. Both are characteristic features of the apparatus. From the vessel C the bent tube g leads into the lower bulb B. The latter through tube 1, and the vessel C through tube 3, both communicate with the atmosphere.

Vessel B is filled through tube 1 so that the level of liquid, the viscosity of which is to be found, lies between marks x and y. Through a tube attached to tube 2 the liquid is sucked up, tube 3 being kept closed with the fingers, so that vessel C, capillary 4, and the upper bulb A are successively filled. The apparatus then presents the appearance shown in Fig. 1. If tube 2 is now opened and, immediately afterwards, tube 3, air enters the apparatus through tube 3 into the vessel C, and divides the liquid into two parts, bringing it to the position shown in Fig. 2. A thin fluid layer with a flat surface is at once formed in the horizontal plane at the lower end of capillary 4. The free surface of this layer faces downwards. In this layer the "suspended level" is set up and, for all liquids which wet, occurs in the same place. Simultaneously with the appearance of the suspended level, the fluid commences to flow from A through the capillary. Vessel C, however, does not fill, but the fluid moves in a thin layer down the vertical side of the vessel and unites with the liquid in g and B. The observer has only to note the time for the meniscus of the liquid to fall from mark m_1 to mark m_2. The method of working is thus simple.

The viscosity in centistokes is obtained in the following manner from the outflow time. The latter, in seconds, is multiplied by the particular calibration constant etched on the capillary.

For the narrowest capillary		(0·63	mm.	diameter)	= 0·01.†
,, ,, middle	,,	(1·13	,,	,,)	= 0·10.
,, ,, widest	,,	(2·01	,,	,,)	= 1·00.

* Paper received October 12th, 1935. Translated from the German by Dr. W. E. J. Broom.

† Sometimes the calibration constant departs from the above by a few tenths of 1 per cent., which can be disregarded for routine work.

Thus, the capillary constant is always a power of ten, so that only a decimal must be moved in the outflow time in order to obtain the kinematic viscosity in centistokes.

The viscometer is provided with a metal cage consisting of two end plates joined by three tie-rods. The cage affords protection against damage.

The Thermostat (Heating-bath).

Three similar viscometers, each with its protecting cage, hang in a common bath vessel of Jena glass, which is full of water. The vessel is closed in at the top with a lid which contains the necessary openings for the viscometers, the electric stirrer, the heating element, and the thermo-

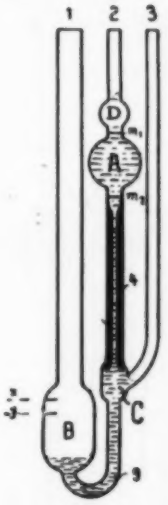


Fig. 1.

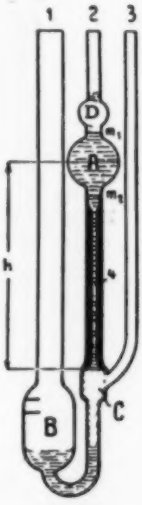


Fig. 2.

regulator (see Fig. 3). Heating and temperature control * are electrical, the latter by means of an adjustable contact thermometer. The bath vessel is enclosed at a distance of 3 cm. by an outer metal case, which is fitted with a narrow glass window for observation of the capillary. The space between the outer case and the bath is filled with crumpled aluminium foil in order to provide good heat insulation.

In addition, with the thermostat just described one can obtain so good temperature regulation that it is permissible to submerge the cage in the bath liquid up to the level of the top plate.

New Temperature Bath.[2]

When the temperature viscosity relationship is known, it is no longer necessary to work at the usual temperatures, *e.g.* 50 or 100° C., and it is

* All electrical connections were led together through a single conduit.

more convenient to heat the viscometer, or other measuring instrument, with the vapour of a liquid. For example, the viscometer may be suspended in the vapour of boiling benzene, when it very soon acquires the temperature of the benzene vapour.

In the new temperature bath the ascending vapours are condensed on a cold surface, which is situated above that part of the apparatus which is filled with the material under investigation.

When a liquid is heated in a vessel, the vapour from the boiling liquid rises, and a ring of condensation is seen on the walls and creeps slowly

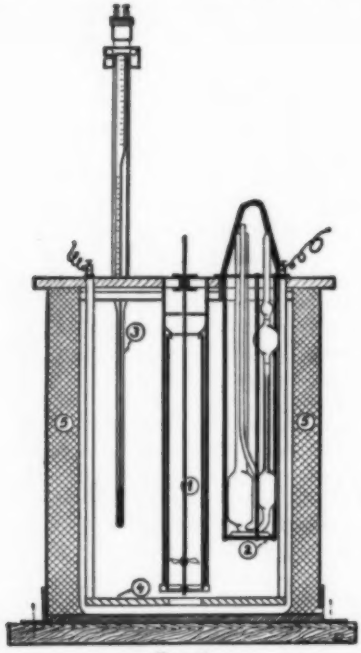


FIG. 3.

upwards. If a metal casing with a cooling liquid flowing through it is hung in a cylindrical vessel (see Fig. 4), the vapour is condensed on its underside. This phenomenon has already been utilized in many cases with the so-called "Pilzkühlern." In this particular case, the ring-shaped casing is a loose fit in the vessel, and, moreover, the viscometer is supported loosely on a ring inside the condenser (see Fig. 4).

Even when the liquid in the vessel is allowed to boil freely, practically no vapour passes through the existing openings, and little is lost.

In order to prove that the temperature was equal throughout the whole vapour space, the temperature over various boiling liquids was measured at different heights in the vessel. This demonstrated that, as mentioned before, with the liquid briskly boiling, the whole vessel being filled with vapour and a reasonable amount of liquid dropping back from the con-

denser, the temperature, *e.g.* using boiling benzene, at 2 cm. above the boiling liquid and 1 cm. below the condenser, varied by not more than 0·1° C. The boiling points of liquids are known to depend on the atmospheric pressure. Therefore, the temperature in the vapour space must be measured with an accurate thermometer for each experiment, and indeed it is expedient that the whole mercury thread should be immersed in the vapour. Otherwise, the correction for the exposed stem must be taken into account. As bath liquids may be used: Acetone, 56° C.; methyl alcohol, 65° C.; carbon tetrachloride, 77° C.; benzene, 80° C.; toluene, 111° C.; xylene, about 140° C.; pseudo-cumene, 168° C.; aniline, 184° C.; nitrobenzene, 211° C.

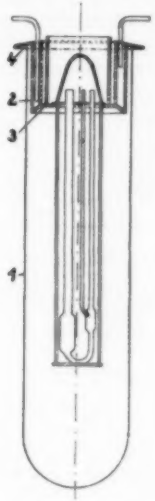


FIG. 4.

Water is not suitable as the bath liquid, since a mist is formed in the upper vapour space, which has a lower temperature. This is perhaps due to the higher surface tension of water.

The temperature bath can also be used for keeping the viscometer, etc., at a constant temperature of 20° C., or at room temperature. The bath is filled with water and brought to the desired temperature by heating or running in cold water. The heat capacity of the requisite water mixture suffices to keep the temperature constant during a usual experiment. Working in this way, this single temperature bath will cover all viscosity measurement.

THE HAGENBACH CORRECTION.

To ascertain if the Hagenbach correction term m was contained in the formula for the determination of viscosity from outflow time and apparatus constant.

$$v = \frac{\pi g h r^4}{8lV} \cdot t \cdot - \frac{mV}{8\pi l t}$$

where v = viscosity in centistokes,
g = gravitational constant,
h = mean head,
r = radius of capillary,
l = length of capillary,
V = volume of fluid run out,
t = outflow time.

In the first publication on the suspended level viscometer, it was fully pointed out that the value[3] of $m = 1{\cdot}12$, *i.e.* the value theoretically derived and used by many workers, gave large corrections. This fact is not surprising, since the value 1·12 is valid only for a capillary cut off at right angles, whilst the capillary of the suspended level viscometer is not cut off in this way, but expanded into a funnel shape. For each of the capillaries of different diameters, the outflow times of water and of a gas

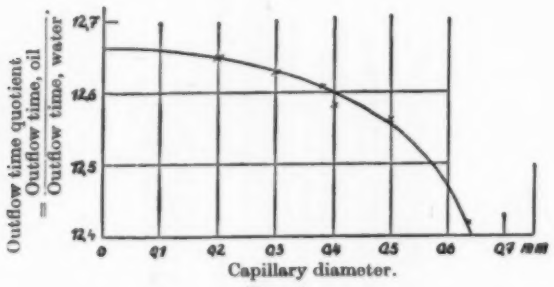


FIG. 5.

oil of viscosity about 12 centistokes have been determined. The quotient, $\frac{\text{outflow time of oil}}{\text{outflow time of water}}$, plotted against the capillary diameter gives a curve that cuts the vertical axis (Fig. 5). The point of intersection gives the theoretical outflow time quotient (where the kinetic energy correction, and thereby the Hagenbach correction, are infinitely small). The outflow times of capillaries of finite dimensions are in this way corrected, so that the quotient obtained is corrected to the "infinite" value.

Let Q = theoretical quotient,
t_w = water outflow time in any capillary,
t_0 = oil outflow time in the same capillary,
x = corrected water time in the capillary.

Then x is found from:

$$Qx = t_0 - \frac{t_w - x}{Q}$$

whence

$$x = \frac{Qt_0 - t_w}{Q^2 - 1}$$

From the measured time of outflow for water, t_w, is subtracted $\delta = t_w - x$. Thence follows the value for m from the relation,

$$m = \frac{8\pi l \delta k t_w}{100 V}$$

where k = the viscometer constant.

In this way, from the plotted data in Fig. 5 the determined value for m is 0·80.

TABLE I.

Capillary diameter, mm.	Measured outflow time/secs.		Outflow time, quotient.		
			Uncorrected.	Corrected with	
	Water.	Oil.		m = 1·12.	m = 0·8.
0·63	103·4	1,284	12·42	12·74	12·66
0·50	233·1	2,927	12·56	12·69	12·66
0·40	501·5	6,310	12·58	12·66	12·64
0·38	860·0	10,846	12·61	12·65	12·64
0·30	1918·0	24,226	12·63	12·65	12·65
0·20	5052·0	63,908	12·65	12·66	12·66

Table I shows that the variation of the corrected outflow time quotient with increasing capillary diameter is only very slight, with the value of m = 0·80, whilst with m = 1·12 the deviations are clearly greater.

Based on this data, Table II was calculated for the Hagenbach correction.

TABLE II.*

Correction Table for the Hagenbach Correction.

With the italicized figures, an error of not more than ±0·1 per cent. is obtained. With those figures not italicized the maximum error is ±0·2 per cent. The figures in parentheses exceed these limits.

Observed outflow time/ secs.	Corrections in secs. to be subtracted from the outflow time for capillary.			Observed outflow time/ secs.	Corrections in secs. to be subtracted from the outflow time for capillary.		
	I.†	II.	III.		I.†	II.	III.
20	(10·00)	(1·00)	*0·10*	100	2·00	*0·20*	*0·02*
25	(8·00)	0·80	*0·08*	120	*1·67*	*0·17*	*0·02*
30	(6·67)	0·67	*0·07*	140	*1·43*	*0·14*	*0·01*
35	(5·72)	0·57	*0·06*	160	*1·25*	*0·13*	*0·01*
40	(5·00)	0·50	*0·05*	180	*1·11*	*0·11*	*0·01*
45	(4·45)	*0·45*	*0·04*	200	*1·00*	*0·10*	*0·01*
50	(4·00)	*0·40*	*0·04*	250	*0·80*	*0·08*	—
55	(3·64)	*0·36*	*0·04*	300	*0·67*	*0·07*	—
60	(3·34)	*0·33*	*0·03*	350	*0·57*	*0·06*	—
70	(2·86)	*0·29*	*0·03*	400	*0·50*	*0·05*	—
80	2·50	*0·25*	*0·03*	450	*0·45*	*0·04*	—
90	2·22	*0·22*	*0·02*	500	*0·40*	*0·04*	—

* This table is also given in "Zur Viscometrie." [1]

† The capillaries labelled I, II, and III refer to capillaries with calibration constants of k = 0·01, 0·1, and 1·00. (The table is also valid when k departs a little from these values.)

Surface Tension.*

The viscometers are calibrated with mineral oil and, therefore, the calibration constant k so determined is valid only for liquids of similar surface tension and density. Otherwise a correction is brought in.

Owing to surface tension, a small column of liquid is drawn up at the higher level, *i.e.* in the measuring bulb. This varies greatly with the alteration in the diameter of the meniscus, as the fluid runs down and head is actually lost. At the suspended level itself the surface tension has no effect, as a complete discharge of pressure is produced, and the case in the bulb must only be considered.[4] † For this object, the Poiseuille equation is written,

$$t = \frac{kV}{h} \quad \text{where} \quad k = \frac{8lv}{\pi g r^4}$$

So in regard to surface tension is written,

$$t' = \frac{kV}{h - \Delta h}$$

where Δh is the column of liquid drawn up by surface tension. The difference between the outflow times of two liquids of equal viscosity, but one of infinitely small and the other of definite surface tension, is,

$$\Delta t = kV\left(\frac{1}{h - \Delta h} - \frac{1}{h}\right) = \frac{kV}{h} \cdot \frac{\Delta h}{h - \Delta h}$$

Δh is small compared with h, and can be neglected in the denominator, so that

$$\Delta t = \frac{kV\Delta h}{h^2}$$

and

$$\frac{d\Delta t}{dV} = \frac{k\Delta h}{h^2}$$

Let

γ = surface tension,
g = gravitational constant,
ρ = fluid density,
D = meniscus diameter,
R = bulb radius,
x = the distance the liquid meniscus has travelled on its path. (See Fig. 6.)

Thus from the known formula for capillary rise,

$$\Delta h = \frac{4\gamma}{Dg\rho}$$

wherein $D = 2\sqrt{2Rx - x^2}$ and $dV = dx \,.\, \pi \,.\, (2Rx - x^2)$.

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* According to a personal communication from Prof. Ubbelohde he has now succeeded, by means of a small alteration to the viscometer, in obviating the necessity for a surface tension correction.—W. E. J. B.

† Barr has calculated this value already for a given case, but did not derive a generally applicable formula.

Hence it follows,

$$\Delta t = \frac{2\pi k\gamma}{h^2 g\rho} \int_0^{2R} dx\sqrt{2Rx - x^2} + c$$

$c = 0$, therefore $x = 0$, also $\Delta t = 0$.

The function under the integral sign is the equation of a circle of radius R. That is,

$$\Delta t = \frac{2\pi k\gamma\pi R^2}{h^2 g\rho} = \frac{2\pi^2 R^2 k\gamma}{h^2 g\rho}$$

and

$$t = \frac{kV}{h} \text{ and } V = \frac{4\pi R^3}{3}$$

So it follows

$$\frac{\Delta t}{t} = \frac{1{\cdot}5\pi\gamma}{hg\rho R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

There still remains to be calculated the effect of surface tension on the upper and lower tubes, attached to the bulb, which carry the timing marks. If d is the internal diameter of these tubes,

$$\frac{\Delta h}{h} = \frac{\Delta t'}{t'} = \frac{4\gamma}{dg\rho h}$$

The volume of the bulb is V, and that of the ends of the tube V', where V' and t' are both small compared with V and t, so to a first approximation,

$$\frac{\Delta t'}{t} = \frac{V'}{V} \cdot \frac{4\gamma}{dg\rho h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This, brought in, gives a total correction,

$$\frac{\Delta t + \Delta t'}{t} = \frac{1{\cdot}5\pi\gamma}{hg\rho R} + \frac{4V'\gamma}{hg\rho dV} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This relation has been tested experimentally. To the same capillary two bulbs of different diameters were fixed, and in this way the bulb diameter, but no other part of the apparatus, was altered.

With each of these arrangements the outflow times of water ($\gamma = 73$ dynes/cm., $\rho = 1{\cdot}0$ gm./cm.^{3}) and cumene ($\gamma = 34$ dynes/cm., $\rho = 0{\cdot}8$ gm./cm.^{3}) were measured and then were corrected by the use of equation 3.

The outflow time quotient must be equal with all such arrangements. Taking into account the higher experimental error of these experiments, owing to their difficulty, the equation is established and experimentally certified.

As an illustration, the calculation of one experiment follows. The dimensions of the apparatus with the usual (small) bulb were $R = 1{\cdot}1$ cm., $h = 13$ cm., $d = 0{\cdot}4$ cm., and the length of each portion of the tubes attached to the bulb, $L = 2{\cdot}0$ cm. The correction for the water outflow time amounts to

$$\frac{\Delta t}{t} = \frac{150 \times 3{\cdot}14 \times 73}{13 \times 981 \times 1 \times 1{\cdot}1} + \frac{0{\cdot}25 \times 73 \times 400}{5{\cdot}45 \times 0{\cdot}4 \times 981 \times 13 \times 1} = 2{\cdot}62\%.$$

For cumene the correction amounts to

$$\frac{\Delta t}{t} = \frac{150 \times 3{\cdot}14 \times 34}{13 \times 981 \times 0{\cdot}8 \times 1{\cdot}1} + \frac{0{\cdot}25 \times 34 \times 400}{5{\cdot}45 \times 0{\cdot}4 \times 981 \times 0{\cdot}8 \times 13} = 1{\cdot}57\%.$$

The outflow time of the water amounted to 1917 seconds. After application of the correction, this becomes 1867 seconds. Similarly, for cumene, the outflow time of 1912 seconds becomes 1882 seconds. Hence the outflow time quotient

$$Q = \frac{1882}{1867} = 1{\cdot}008.$$

With the larger bulb, $R = 2{\cdot}41$ cm. and $L = 0{\cdot}7$ cm., with other dimensions remaining the same, the corrections to be applied to the

FIG. 6.

observed outflow times of water and cumene, which were 18,751 and 18,867 seconds, respectively, calculated out as 1·14 and 0·67 per cent., respectively. Hence the corrected times were 18,537 and 18,741 seconds, giving an outflow time quotient of

$$Q = \frac{18{,}741}{18{,}537} = 1{\cdot}011$$

That the values of Q differ by 3 parts in a thousand is ascribed to the difficulty of the experimental technique.

It can be seen further that the determination of the viscosity of cumene carried out in the normal viscometer (with a small bulb) would lead to an error of 1·05 per cent., if the viscometer was previously calibrated with water and the deduced correction not applied.

As mentioned, the viscometer is calibrated with mineral oil, and if used only for the viscometry of similar oils, the correction can be disregarded. For application when other liquids are examined, a correction table has

been calculated. For this purpose the apparatus dimensions (h and R) of the suspended level viscometers now in use were introduced into equation 3, so that the expression obtained is:

$$\frac{\Delta t}{t} = 0{\cdot}000371\,\frac{\gamma}{\rho}$$

With the help of this equation, the correction value for a liquid under examination is found and subtracted from the correction value for mineral oils (γ = (about) 30 dynes/cm. and ρ = (about) 0·88 gm./cm.[3]). The difference is either added to or subtracted from unity according to its sign.

The factor so obtained is multiplied by the determined viscosity. These factors are collected in Table III for the range of surface tensions and densities in question.

TABLE III.

Correction Table for Surface Tension.

Surface tension divided by specific gravity.	Multiply measured viscosity by
20	1·0052
30	1·0015
40	0·9978
50	0·9941
60	0·9904
70	0·9867
80	0·9830
90	0·9792
100	0·9755

References.

[1] *J.I.P.T.*, 1933, **19**, 376; *Proc. World Petr. Congr.*, 1933, **2**, 496; "Zur Viskosimetrie," L. Ubbelohde, Verlag Mineralölforschung, Berlin. 1935.

[2] Ubbelohde and Walther, *Öl u. Kohle*, 1935, **11**, 610.

[3] Erk, "Viscosity Measurement and Liquids." Forschungsarbeiten V.D.I., 1927, No. 288.

[4] Barr, "Viscosity and its Expression," *Proc. World Petr. Congr.*, 1933, **2**, 508.

THE BALL AND BUCKET VISCOMETER.

By E. S. L. Beale and P. Docksey (Associate Member).

Viscometers may be divided into two general classes—absolute viscometers in which the constant for converting the readings to absolute units can be calculated from the dimensions of the apparatus, and practical viscometers in which the constant must be determined experimentally from measurements on liquids of known viscosity. The apparatus under discussion belongs to the latter class.

The essential feature of any practical viscometer is that it should give accurately repeatable readings of viscosity when measuring the viscosity of a given liquid at a fixed temperature, and that it shall be convenient to use when measuring the viscosity of liquids of the type for which it is intended.

The principal object of the present design is to provide a simple apparatus which will measure the viscosity of liquids over a wide range of viscosities and temperatures with fair accuracy and good repeatability, an apparatus which requires only a small quantity of oil for its operation, and which is readily adaptable to semi-automatic recording, in the sense that it can easily be made to actuate a stop-clock to record the time of operation. The apparatus is also well suited to the measurement of the consistency of waxy oils, asphalt containing solid matter in suspension, paints, varnishes, printers' ink, glue and all similar materials which do not possess a true viscosity but for which a reliable measure of consistency is needed.

The present design consists of an adaptation of the well-known "falling sphere" viscometer. As usually constructed, a steel or heavy metal ball is allowed to fall freely in the liquid under examination, which is contained in a vessel of suitable dimensions. If the containing vessel is very large compared with the steel ball, the constant can be calculated from the size and weight of the ball by Stokes' Law. If the vessel is not much larger than the ball—as, for instance, if it takes the form of a tube with just enough clearance to allow the ball to fall or roll freely—the constant can only be calculated with difficulty, but this forms a useful practical viscometer.

By adjusting the clearance between the ball and the bore of the tube, this form can be made suitable for oils of greatly different viscosities. The chief objection to this type is the difficulty of observing the rate of fall of the ball, particularly in the case of black oils. In the present apparatus the usual arrangement is reversed (Fig. 1). The steel ball is supported mechanically, and the tube, the bottom of which is closed, surrounding the ball and containing the oil is allowed to fall under its own weight. In this way the relative motion of the tube and the ball can readily be observed. The tube containing the oil will henceforth be referred to as the "bucket."

Another advantage of this arrangement is that it is a simple matter to make the bucket fall away freely from the ball after an accurately specified travel by enlarging the bore of the bucket at a suitable point, thereby greatly reducing the resistance to motion beyond that point. The sudden

release of the bucket can clearly then be used to indicate the time after the start taken for this well-defined relative motion, and also, if required, to operate a stop-clock by falling on a suitably placed mechanical linkage, and this is a particularly useful feature when the time of fall is long, as no attention need be given to the apparatus after the start. For this reason it has been found very useful for plant control in cases where the viscosity of one of the products is of importance, and where the operator in control of the plant may not have much attention to give to the apparatus.

There is a well-known viscometer, known as the Michell viscometer, in which the steel ball falls from an inverted cup, thereby indicating the end of the operation. The disadvantage of this arrangement is that the ball itself may become mechanically damaged by the impact, whereas in the present design only the outside of the bucket would be damaged, and the exact shape of this is of no consequence. Furthermore, by using a much

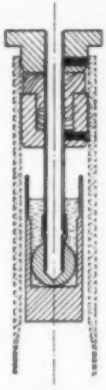

Fig. 1.

larger quantity of oil than in the Michell viscometer, the exceedingly fine clearances can be avoided, thereby making the readings very much more repeatable in the presence of minute quantities of impurity in the oil, and conferring other obvious advantages in construction.

By providing a number of balls of slightly different diameter, the constant of the apparatus can be changed to suit liquids up to extremely high viscosities.

As an example of an apparatus constructed in accordance to this system the following dimensions have been found satisfactory for lubricating oils of medium viscosity :—

	cm.	inch.
Internal diameter of bucket (over calibrated length)	2·00	0·787
Diameter of steel ball	1·98	0·779
Diametral clearance	0·02	0·008
Enlarged diameter of bucket	2·26	0·890
Diametral clearance	0·28	0·100 (approx.)
Length of travel of ball up to enlargement	2·0	0·787
Weight of bucket	93·15 grm.	
Volume of oil required	9·25 ml.	

The constant of an apparatus of these dimensions is approximately 3·0. That is to say, the viscosity in centipoises is given by multiplying the time in seconds required for the bucket to fall by 3·0.

Thus :—Centipoises = Seconds × 3·0.

Viscometers of this type can be made with constants larger or smaller than this simply by altering the size of the ball used in a given sized bucket or vice versa. For instance, an instrument similar to the above has been constructed with a clearance of 0·014 inch on the diameter which gives a constant of about 14, and is therefore suitable for bright stock at 100° F. and bitumens at higher temperatures. It is also possible, by reducing the clearance to about 0·003 inch, to make a viscometer with a constant of about 0·3. This will provide a viscometer covering the same range as the Redwood I Instrument, but with rather greater accuracy over the whole range, particularly at low viscosities.

It is found, in accordance with simple theory, that the value of the constant is proportional to the clearance to the power 2·5, and on this basis five instruments have been designed, particulars of which are given in the table below, to cover the whole range of viscosities for which this type of apparatus is suitable.

Diametral clearance.	Constant.	Viscosity (centipoises) for various times.			
		5 secs.	30 secs.	300 secs.	1000 secs.
inch					
0·003	0·3	1·5	9	90	300
$0{\cdot}006_5$	2·0	10	60	600	2,000
$0{\cdot}014_5$	15·0	75	450	4,500	15,000
0·031	100	500	3,000	30,000	100,000
0·078	1,000	5,000	30,000	300,000	1,000,000

For a time of fall of 30 seconds, which represents the lower limit for reasonably accurate work, the error due to $\frac{1}{2}$ second is only 0·66 per cent.

The upper limit of viscosity which can be measured is only set by the time available if the temperature control can be relied on, since the experiment can be started and allowed to finish by itself. For instance, with an instrument having a constant of 1000, if the experiment could be allowed to run overnight, a viscosity of 50,000,000 centipoise could be recorded (time of fall 14 hours).

The column headed 5 seconds is intended to indicate the lowest viscosity for which a rough measurement can be obtained, since an error of $\frac{1}{2}$ of a second is equivalent to a 4 per cent. error on the time, and therefore on the viscosity, as the two are accurately proportional on this type of instrument. Actually, since repeat readings can so easily be made with the apparatus, results very much more accurate than these figures indicate can be obtained by averaging a number of determinations.

A rough comparison can be drawn between the Ball and Bucket having a constant of 0·3 and the Redwood I Instrument. An error of $\frac{1}{2}$ second with the automatic timing on the ball and bucket might be said to correspond to an error of $\frac{1}{2}$ second on the Redwood I, and using this basis for comparison,

we get the following percentage errors in the measured viscosity due to the timing error for oils of different viscosities :—

Viscosity (centipoises).	Redwood I.		Ball and Bucket (Const. = 0·3).	
	Seconds.	Error on Visc.	Seconds.	Error on Visc.
		Per cent.		Per cent.
1·5	30	15·5	5	4·0
3·6	35	5·8	12	1·67
9·0	49	1·9	30	0·67
24	100	0·6	80	0·25

On this showing, the ball and bucket is considerably more accurate than the Redwood I viscometer, particularly at low viscosities, but it should be realized that this is not by any means the only factor which should be taken into account in estimating the overall accuracy of a viscometer.

To mention one point only of basic importance, the flow in the annular space between the ball and the bucket is, by calculation, safely in the viscous region. Even with an oil of low viscosity, 1·5 centipoise, and the shortest time of fall, 5 seconds, the calculated value of the Reynolds Number is less than 25, and turbulence may be expected only at Reynolds Numbers over 1000.

The bucket is made with truly cylindrical bore, and the ball is made as nearly spherical as possible, and accurately circular at the horizontal great circle; the error due to different relative positions is thus minimized. The materials used for the construction of each should be very hard to avoid abrasion, and non-corrodible. Hardened stainless steel is very suitable, and in order to avoid substantial change in constant due to differential expansion between the ball and the bucket, they must both be made of exactly the same material, and preferably from the same billet.

The exact value of the constant clearly depends on the specific gravity of the oil and the way the viscometer is used. If the bucket falls in air, the force causing the motion to take place is the weight of the bucket plus a certain fraction (approximately half) of the oil contained in it. A correction to the constant could be applied for differences in the specific gravity of the oil, but for many purposes the error involved in assuming it to be 0·900, whatever oil is used, is small enough to be neglected. This error in the case of oils having a range of specific gravity of 0·800 to 1·000 is less than $\pm$ 0·5 per cent.

If the bucket is immersed in a large quantity of the oil under test, the force causing the motion to take place is the weight of the bucket minus the buoyancy of the oil displaced by it. This constant will be slightly smaller than that for use in air, and will also depend to a small extent on the specific gravity of the oil, but the variation can again often be neglected, as over the range of specific gravity mentioned previously the error is less than $\pm$ 1·5 per cent.

For making accurate measurements of viscosity, particularly of high viscosity liquids, it is essential that the temperature of the liquid should be constant during the determination and accurately known. For this

purpose the Ball and Bucket is surrounded by a temperature-controlled enclosure of usual type, and the temperature of the inside of the ball is taken by means of a thermometer passing down the hollow supporting-rod

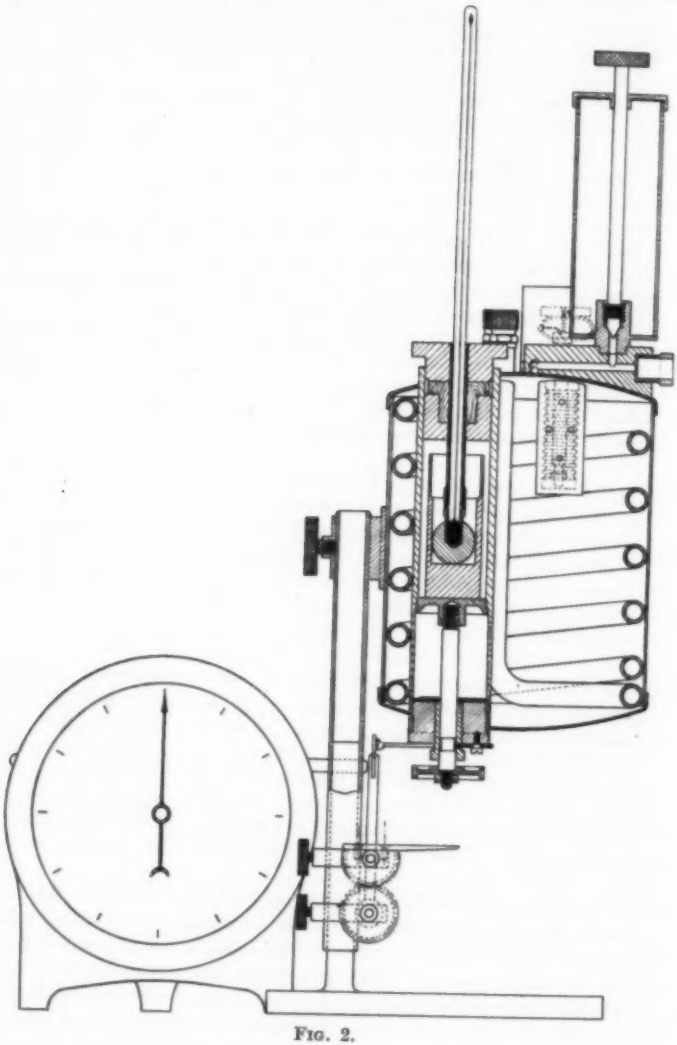

FIG. 2.

of the ball, so that the bulb of the thermometer is at about the middle of the ball. When this thermometer and that in the constant-temperature bath surrounding the bucket show the same temperature, it may be assumed that

the oil in the bucket has reached a uniform temperature—namely, that of the ball.

One very important feature of the design is that the thermometer inside the ball gives a definite indication of the temperature of the oil. An accurate indication cannot be obtained in many viscometers in normal use—for instance, in a viscometer of the Ostwald type the only means of making sure of the temperature of the oil is to make repeat determinations.

A convenient means of bringing the whole to the same temperature as the constant temperature enclosure without the necessity of immersing the bucket in any liquid, is to arrange the bucket to work in a vertical tube with adequate clearance all round, the tube being surrounded by a water bath.

The disadvantage of this arrangement is that rather a long time is required for the apparatus to reach the same temperature as the bath (of the order of 40 minutes to get to within 1° F.). Although the air-jacket suffers from slow heating up, at the same time it offers the advantage that with a reasonably small temperature difference (about 0·5° F.) a determination can be carried out without the temperature changing enough to vitiate the experiment. By arranging that there shall be good metallic contact between the bottom of the bucket and the metal surface in direct contact with the bath when the viscometer is not actually in operation, the time can be reduced to between one-half and one-third. If the temperature of the bath can be adjusted over a range of a few degrees, the heating-up period can be very greatly reduced.

A convenient design of thermostat incorporating these features is shown in Fig. 2, which also shows one form of trigger device for stopping a stop-clock at the end of the time of fall. In this design the bath is completely closed, and is filled with a suitable oil. The expansion of the oil operates a mercury switch through a metal bellows. The whole acts, therefore, as its own thermo-regulator. By distributing the electrical heating and preventing vertical convection currents by packing the bath with copper wire, a substantially uniform temperature is attained without the use of a mechanical stirring device.

In addition to the measurement of the viscosity of true liquids, a very useful measure of the consistency of paints, varnishes, glue, printers' ink and any such emulsion or suspension which does not possess a definite viscosity at a given temperature can be obtained. In such cases the apparent viscosity depends on the rate of shear, so that a different value would be obtained if tested in two viscometers with different constants. However, the Ball and Bucket provides a very simple and convenient apparatus for the control of the consistency of such materials, and gives good repeatable readings under given conditions.

In conclusion, it may be worth mentioning briefly some of the valuable features of this type of viscometer not already mentioned.

The apparatus is easily cleaned and very easily filled, since the precise quantity of oil in the bucket is of no great importance (as long as there is enough). No particular care in levelling of the apparatus is needed, since the bucket is bound to hang vertically from the ball in any case. There are no drainage or surface tension effects, and since the timing is purely mechanical there is no difficulty due to the opacity of black oils.

There is no particular limit to the temperature range over which the Ball and Bucket may be used. For instance, with a suitable constant-temperature bath, temperatures up to 400° F. should be quite practicable with non-volatile oils, and temperatures down to say — 40° F. or lower could be used in connection with dewaxing operations without any difficulty. At temperatures below the dew point of the surrounding air, water vapour is liable to condense on the bucket, but since the weight of the bucket is about 100 grm., quite a substantial amount of condensation can be allowed without appreciably affecting the constant of the viscometer.

The great ease with which repeat determinations can be made, the excellent repeatability of the results ($\pm$ 0·1 per cent.), and also the fact that no judgment on the part of the operator is required in order to determine the end of the timed period, all contribute towards making the viscometer much more accurate than one might expect, particularly at short times of fall. The trigger device for stopping the stop-clock makes it more suitable than probably any other viscometer for the measurement of high viscosities with very long times of fall.

The authors' thanks are due to the Chairman of the Anglo-Iranian Oil Company for permission to publish this paper.

CORRESPONDENCE.

To the Editor,

SIR,—In Mr. W. C. Woolgar's paper entitled "The Viscosity and Stability of Drilling Fluid" (*Journal*, 1935, p. 825) the name Kamlial is throughout spelt Kamilal. This name denotes an important "key" formation in the North-West India Tertiary sequence; it was proposed by Mr. E. S. Pinfold, and is universally accepted as part of the standard nomenclature of this area, as may be seen from the various Geological Survey of India and other publications dealing with the Punjab Tertiaries. Its appearance in a mutilated form may give rise to confusion.

Yours faithfully,

P. EVANS.

Rawalpindi,
November 19th, 1935.

COMPUTATIONS FOR COUNTER-CURRENT SOLVENT EXTRACTION PROCESSES.*

By T. G. Hunter, B.Sc., A.R.T.C., A.I.C., and
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Computations for counter-current contact processes for the extraction of a solute from a liquid by means of a second liquid have been thoroughly described in the literature.[1, 2] When equilibrium relationships in a complex hydrocarbon-solvent system are represented graphically on triangular co-ordinates, certain graphical computation methods may be used with fair success for this case. Although these equilibrium representation and graphical computation methods have been discussed separately in the literature, they have not so far been presented together.

This paper is therefore a brief description of a computation method suitable for application to the process of counter-current refining of petroleum products by means of selective solvents, and is essentially a survey of our own work on this subject already published elsewhere.

Equilibria in Complex Hydrocarbon-Solvent Systems.

Where solvent extraction is employed for the removal of undesirable constituents from petroleum products, such as the extraction of aromatics from kerosine by liquid sulphur dioxide and the refining of lubricating oils by selective solvents, the equilibria involved cannot be represented exactly by any simple means. Exact representation could only be obtained by the use of complex methods involving a comprehensive knowledge of the constituents of such products. However, the problem is simplified by our ignorance of the chemical nature of petroleum products, and equilibria characterization on the following lines leads to an approximate solution.

In the solvent refining of an oil, the solvent tends to split the oil into two fractions, soluble and less soluble, possessing different physical characteristics. These two fractions do not represent a sharp separation of the oil into purely soluble and less soluble constituents, but are mixtures of both. In certain special cases the nature of the soluble and less soluble constituents may be known, as, for example, in the refining of kerosine, where the more soluble constituents are aromatic hydrocarbons and the less soluble non-aromatic. In such a case, where the amounts of aromatic and non-aromatic hydrocarbons are readily determined by analysis, then, the oil may be considered as a simple two-component system, the two components being each complex mixtures of aromatic and non-aromatic hydrocarbons, respectively. The resulting oil-solvent system may then be treated as a simple ternary system, and equilibrium relations represented on triangular co-ordinates in terms of solvent, aromatics, and non-aromatics.[3] Cases where the oil can be analysed in terms of two groups of

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constituents are, however, relatively rare and unimportant, compared with cases where such analysis is impossible.

The chemical nature of the hydrocarbon groups present in any lubricating oil, for instance, is not known. Such oils are usually considered to be made up of two major groups of constituents, generally referred to as naphthenic and paraffinic, where the term naphthenic is to be interpreted as denoting a mixture of hydrocarbon groups relatively poor in hydrogen, and the term paraffinic as a mixture of hydrocarbon groups relatively rich in hydrogen. The groups comparatively poor in hydrogen form the bulk of the undesirable constituents which have to be removed to produce a good lubricating oil, and possess a high value for the viscosity gravity constant (V.G.C.) and a low value for the viscosity index (V.I.), whilst conversely the desirable or so-called paraffinic constituents have respectively low and high values for these two physical properties. The degree of refining of a lubricating oil stock may, therefore, be followed and controlled to a certain extent by the use of these or similar physical properties.

Therefore with our present state of knowledge, in order to represent the equilibrium relations in an oil-solvent system, it is only necessary to record by some suitable means the following information:

(1) Amounts of the two phases in equilibrium.
(2) Amount of solvent in each phase at equilibrium.
(3) A physical property of the oil present in each phase at equilibrium.

Items (2) and (3) of this information can be recorded by a single point on a triangular graph of which one vertex represents pure solvent and one side, opposite to this vertex, is scaled into units representing the required physical property of the solvent free oil.[4] The equilibrium resulting between a lubricating oil and nitrobenzene at 10° C. is shown in Table I.

TABLE I.

Lubricating Oil Stock A and Nitrobenzene at 10° C.

Expt.	Ratio of Solvent to Oil used.	Raffinate Layer.			Extract Layer.		
		% Original Oil in Layer.	V.G.C. of Oil in Layer.	% Solvent in Layer.	% Original Oil in Layer.	V.G.C. of Oil in Layer.	% Solvent in Layer.
1	6	10·5	0·824	10·7	89·5	0·872	87·0
2	3	35·0	0·836	14·6	65·0	0·882	81·9
3	1	63·0	0·851	17·0	37·0	0·900	70·2

These equilibrium relationships are plotted on the triangular graph, Fig. 1. The V.G.C. of the solvent-free oil in the raffinate layer from experiment 1 is given by point *b* on this diagram. Now, if raffinate oil of this V.G.C. were mixed with an amount of nitrobenzene such that the total mixture contained 10·7 per cent. of nitrobenzene, we should get the actual raffinate layer obtained. Therefore by joining *b* to the apex of the triangle representing 100 per cent. of nitrobenzene and locating the point on this line where the nitrobenzene content is 10·7 per cent., we obtain the point *d*, representing the composition of the raffinate layer. This

may be shown in another way. By starting with the raffinate layer of composition *d* and removing all the solvent present, we would obtain point *b* on the diagram, which is solvent-free oil of V.G.C. 0·824. The composition of the various raffinate and extract layers is therefore easily ascertained, and is indicated on this diagram by the points *d*, *f*, *h* and *e*, *g*, *i* for the example quoted in Table I. Returning again to experiment 1, the compositions of the raffinate and extract layers in equilibrium are given by points *d* and *e*. These two solutions are conjugate, and hence may be joined by the tie-line *de*. The completed isothermal binodial curve and tie-lines shown on the diagram then represent the equilibrium relations for this lubricating oil–nitrobenzene system at 10° C.

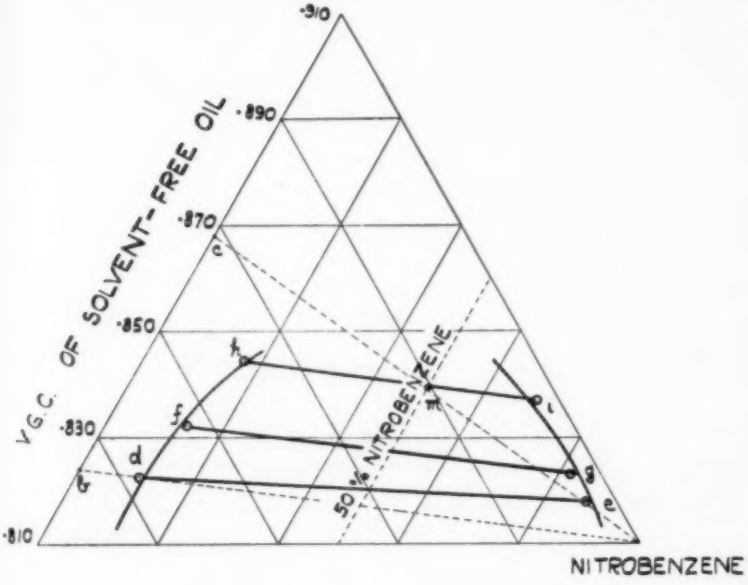

FIGURE 1

This diagram can also be used to determine the amounts of any two phases in equilibrium, given only the quantities of oil and solvent used for the equilibrium experiment. In experiment 3 equal volumes of nitrobenzene and oil were employed, so that the resultant mixture contained 50 per cent. of nitrobenzene, and its composition would be represented by the intersection of the line joining the V.G.C. of the stock, point *c* in the figure, to the 100 per cent. nitrobenzene apex and the line representing 50 per cent. of nitrobenzene—namely, point *m* on Fig. 1. This mixture, however, can only exist as two stable phases in equilibrium the composition *h* and *i* of which is given by the tie-line passing through *m*. The amounts of the raffinate phase *h* and the extract phase *i* are then propor-

tional to the lengths of the two lines *mi* and *mh*. Therefore, knowing the volumes of solvent and oil used originally, the volumes of the two phases formed can be calculated from this relationship. Further, since the volume per cent. of solvent in each phase can be read from the figure, the actual volume of solvent-free oil in each phase can also be calculated. Such a diagram, therefore, gives a complete representation of all essential equilibrium relationships. In constructing these diagrams the scale employed for the physical property of the solvent-free oil can be chosen to give a suitably sized binodial curve. The actual terminal values finally selected become, by the nature of the diagram, equivalent to the physical

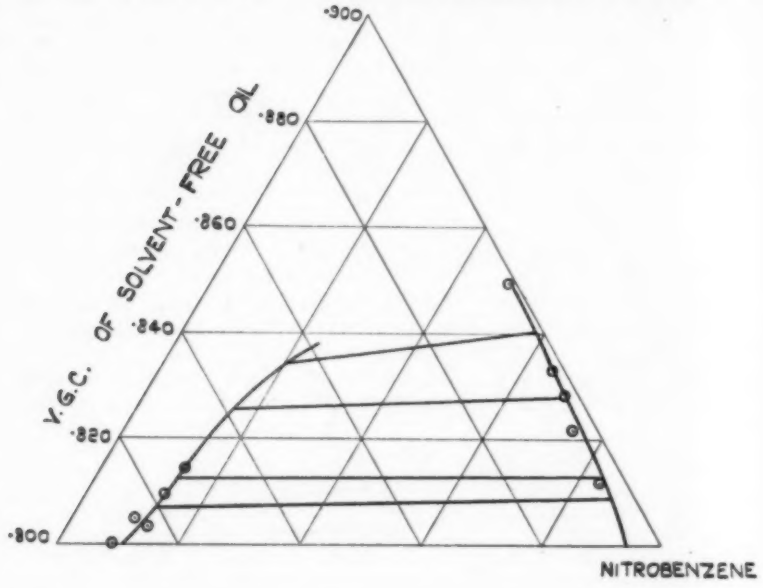

FIGURE 2

property of the soluble and insoluble components of the oil. The physical property chosen for the construction of the equilibrium diagram is also required by the nature of the diagram to be additive.

Such a diagram can best be constructed from experimental results obtained by the single-stage batch extraction of an oil with different volumes of solvent, as in Table I, but care must be exercised to insure that the two liquid phases are in equilibrium.

In a heterogeneous system undergoing agitation, two unstable phases may coexist which are approaching equilibrium with each other. In this case the points representing the composition of each phase at any instant during approach to equilibrium must lie on the binodial curve, since this curve represents the compositions of all possible heterogeneous solutions,

but the tie-line joining two such points would not, of course, represent stable equilibrium. The composition of any phase from a counter-current extraction process would then presumably lie on the binodial curve, even if equilibrium was not attained in each extraction stage.

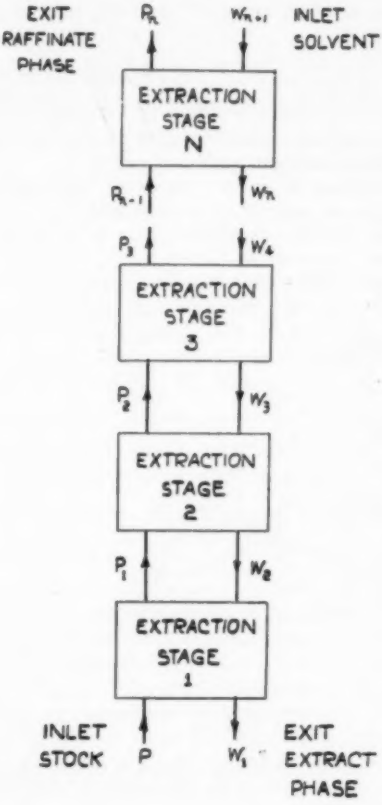

FIGURE 3

In Fig. 2 an oil-solvent equilibrium diagram is given where the equilibrium between nitrobenzene and a semi-paraffinic lubricating oil stock at 10° C. is represented, using the V.G.C. for the physical property of the solvent-free oil.[5] The binodial curve and tie-lines for this system were constructed from batch extraction experiments. The individual points indicated on the figure by circles were obtained by counter-current extraction of the oil with nitrobenzene at 10° C., employing air-agitated extraction stages where equilibrium between the two phases of each stage was probably

not obtained. The fact that these points lie for the most part on the binodial curve affords proof of the previous statement that a point representing the composition of a phase from any extraction stage of an agitated heterogeneous system, whatever the stage efficiency, must lie on the binodial. Such equilibrium diagrams can therefore be employed to compute graphically the results to be expected from any solvent extraction process of oil refining.

Computations for Counter-current Extraction in Complex Hydrocarbon-Solvent Systems.

The triangular equilibrium diagram may be employed as basis for computation in complex oil-solvent systems.[4, 5]

Consider a lubricating-oil stock contacted counter-currently in an isothermal system of n stages with a solvent which is refining the stock by selective extraction where the equilibrium between the stock and the

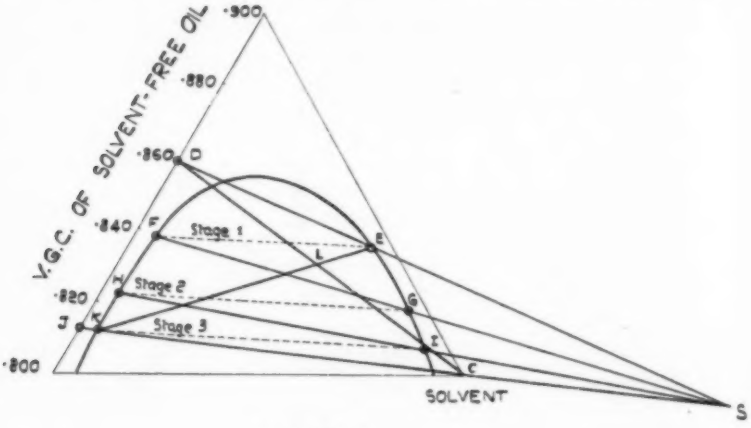

FIGURE 4

solvent is represented by a single binodial curve of the form shown in Fig. 4. Let the amount of stock to be treated entering the system per unit time be P, and the amount of raffinate and solvent phases per unit time leaving any stage be P and W, respectively, each combined with a suffix describing the number of the stage such raffinate solvent or extract phase has just left as shown in Fig. 3.

Computations for such a counter-current extraction process normally involve a knowledge of the value of some physical property of the stock to be treated, the ratio of solvent to stock employed, $\frac{W_{n+1}}{P}$ in Fig. 3, and the value of that physical property of the refined oil desired. Given such data, it is usually required to calculate at fixed working conditions :—

(1) the yield of refined oil,
(2) the amount of solvent associated with the refined oil,

(3) the amount of extract,
(4) the amount of solvent in the extract and yield of solvent-free extract oil,
(5) the value of a physical property of the solvent-free extract oil,
(6) the number of ideal extraction stages required to give the desired refined oil.

In Fig. 4 let points D and J represent the V.G.C. of the treated stock and the desired raffinate, respectively, and the point C the composition of the solvent employed.

The amount of solvent associated with the raffinate is obtained from the point K, where the line joining J and C intersects the binodial curve.

Referring for a moment to Fig. 3 and taking a material balance over the entire system, we have

$$P + W_{n+1} = P_n + W_1$$

That is, the complex obtained by mixing the solvent and stock to be treated can also be obtained by mixing the raffinate and extract streams from the system. It follows that the line joining the two points representing the composition of the stock and solvent streams must intersect the line joining the points representing the composition of the raffinate and extract streams at a point L. Therefore, by joining points D and C in Fig. 4, and dividing the line DC in the ratio $\frac{W_{n+1}}{P}$, we locate the point L, such that $\frac{DL}{LC} = \frac{W_{n+1}}{P}$. By joining point K to L and producing KL to intersect the binodial curve we obtain point E, which represents the composition of the extract, and the ratio $\frac{KL}{LE} = \frac{W_1}{P_n}$.

In an ideal stage, which is the type of stage being considered here, the extract phase leaving a stage is by definition in equilibrium with the raffinate phase leaving the same stage. The composition of the raffinate phase P_1 leaving the first stage is therefore located by the tie-line passing through E, and is the point F in Fig. 4. The point representing the composition of the extract phase W_2 leaving stage 2 must now be located. It has been shown [2] that the point S in Fig. 4 must lie on the line passing through the points D and E, and can be found by the relation $\frac{DE}{ES} = \frac{(P - W_1)}{P}$.

The composition of the extract phase W_2 leaving stage 2 can therefore be obtained from the intersection of the line FS with the binodial at G. Drawing the tie-line through G completes the representation of stage 2. Further construction on these lines enables the number of ideal stages required (three in the case of Fig. 4) to be calculated. Should an auxiliary line passing through point S coincide with a tie-line, no further extraction is possible with the conditions employed.

In Table II the experimental and calculated results from a countercurrent extraction process refining two different lubricating-oil stocks with nitrobenzene at 10° C. are compared.[5] The oil stocks treated were a lubricating-oil stock A, V.G.C. 0·867, and a semi-paraffinic stock V.G.C. 0·853, the equilibrium diagrams of which are given in Figs. 1 and 2.

In arriving at the calculated values in Table II, the yields of solvent-free raffinate and extract oils, the volume per cent. of solvent in both layers, and the V.G.C. of the extract were computed for the treatment of the given

TABLE II.

Counter-current Extraction of Lubricating Oil Stocks with Nitrobenzene at 10° C.

Oil Stock Treated	Volumes of Solvent per 100 Volumes of Oil Stock Used.	Raffinate Layer.					Extract Layer.					
		V.G.C. of Solvent-free Oil.	Solvent-free Oil as Volume % of Original Stock.		Volume % of Solvent in Layer.		V.G.C. of Solvent-free Oil.		Solvent-free Oil as Volume % of Original Stock.		Volume % of Solvent in Layer.	
			Act.	Calc.	Act.	Calc.	Act.	Calc.	Act.	Calc.	Act.	Calc.
Semi-paraffinic Stock V.G.C. 0·853	53·3	0·817	54·8	57·7	14·2	14·0	0·899	0·901	45·2	44·0	49·8	51·0
	100·0	0·811	49·0	50·5	12·5	12·5	0·895	0·897	51·0	49·5	64·8	65·0
	136·4	0·807	44·0	47·5	10·8	12·5	0·889	0·895	56·0	52·5	70·1	71·1
	185·0	0·804	37·7	42·0	12·5	13·0	0·884	0·890	62·3	57·0	74·3	75·5
	375·0	0·799	27·9	23·0	9·0	14·5	0·874	0·879	72·1	72·0	83·7	84·0
Stock A, V.G.C. 0·867	65·0	0·845	56·6	59·3	11·1	16·0	0·897	0·898	43·4	41·4	57·0	56·0
	98·0	0·835	52·5	51·4	13·2	14·0	0·902	0·901	47·5	48·2	65·5	65·0
	188·0	0·831	37·9	40·4	11·2	13·0	0·887	0·891	62·1	60·5	74·7	75·0

stock with the given volume of solvent to obtain a solvent-free raffinate oil having the V.G.C. shown in column 3. The agreement between actual and calculated results is satisfactory and the average deviation is of the order of $\pm$ 10 per cent.

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University of Birmingham.

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[3] Saal and Van Dyck, *World Petr. Congress*, 1933, Vol. 2, 353.
[4] Hunter and Nash, *ibid.*, 340.
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CHARACTERISTICS OF SOLVENT-REFINED MOTOR OILS.*

By Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc. (Member).

SYNOPSIS.

The success of solvent refining lubricating oils is ascribed to improvement in refinery procedure, increase in the potential sources of high-grade products, and improvement in the nature of the products. The latter is regarded as most significant, and is examined in detail in relationship to Pour Point, Carbon Forming Tendency, Viscosity Index and Resistance to Oxidation and Heat. On theoretical grounds it is to be anticipated that the last three would be improved by solvent treatment. Increased resistance to oxidation and thermal stability are by far the most important properties of motor oils. Their behaviour in motor and aircraft engines is believed to follow the course and effect of cracking procedure. It is concluded that the results of heat-oxidation tests actually run parallel to the tendency to form gum and carbon in an engine. Also that such tests will give a better interpretation of improvement in this respect the more severe are the conditions.

The effect in practice of propane–cresylic acid solvent refining on oils from particular sources and on the general standard of commercial motor oils is shown in terms of Viscosity Index, Carbon Residue and Oxidation tests. Extreme paraffinicity as regards viscosity is obtainable in oils from mixed-base sources. As a means of discriminating between oils in respect of their stability, the Air Ministry test has much to commend it for general acceptance, but can be improved by raising the temperature. Measurements have been made up to 250° C., and the results above 220° C. are striking. The increased stability of solvent-refined oils under these severe conditions is very marked.

Mechanical tests measuring Seizing Temperature and variation of Coefficient of Friction with bearing temperature show that solvent-refined oils are in these respects at least as good as the best conventionally-refined oils.

In tests on a glycol-cooled engine run to simulate extreme aircraft conditions, solvent-refined oils give better results than the best ordinary high-quality oils.

General.

The solvent method of refining lubricating oils developed during the last few years and now coming to fruition is one of the big advances in petroleum technology. The general principle of fractionation, or what may better be called partition, of petroleum by means of selective solvents was first applied by Edeleanu to the treatment of the lighter fractions by liquid sulphur dioxide. To-day it has become a tool likely to achieve general application in the hands of the refiner, and one which has already given most noteworthy results in the case of lubricating oils.

Within the last year the headway made by the different process variants of the method has been remarkable. Their widespread adoption speaks more forcibly than anything else of the importance ascribed by the petroleum industry to the manufacture of lubricating oils by solvent extraction. In the United States units have been put into operation or are being built by most of the leading producing companies. In the United Kingdom two large installations are in course of erection, one of them now practically completed and being run in. On the Continent, thanks largely

* Paper presented for discussion at the One Hundred and Sixty-eighth Meeting of the Institution of Petroleum Technologists, December 10th, 1935.

to the high tariff walls, a round dozen plants are in course of construction or have been planned.

The reasons for this striking movement have not been clear even to the oil technologist unless his interests have brought him into immediate touch with the development. To the technical layman knowledge of the advance has come chiefly through the publicity columns of the Press. The facts are that three things have combined to give to the solvent extraction process an importance in the manufacture of lubricating oils not even second to high vacuum distillation.

In the first place, it is a new method of refining—clean, continuous and efficient, which eliminates the use of that bugbear of the refiner sulphuric acid. Had it no other claim to adoption, this alone would have given the method every prospect of success.

Acid treatment losses and the disposal of acid tar are amongst the major problems of refinery operation. Any method which avoided them and had claims to commercial soundness would have been sympathetically received.

Solvent refining is particularly adapted to the treatment of motor and aero oils, because of their high viscosity. With such oils acid can be used only to a limited extent, and sometimes not at all. In the case of solvent extraction viscosity is not a controlling factor, with the result that the heaviest bodied oils are equally well treatable with the lightest.

From the refining angle, however, the great value of solvent extraction lies still more in the fact that it has rendered available for the production of high-class lubricants many crude oils which were either wholly unworked for this purpose or only capable of giving poor yields of low-grade stocks. When the chief properties required in motor oils are examined, it will be seen how important this may be. Many of the less easily worked crudes have become potential sources of such lubricating oils as were previously obtainable only from restricted sources. Close examination of the situation has convinced many producers and refiners that they can now seriously enter the lubricating-oil market; or for the first time even make lubricating stocks to compete with the higher-grade supplies which have been the cream of the production. It is natural that there should be an immediate demand for plants to operate on crudes known to have excellent lubricating fractions hidden in them, but which previously could not even in the laboratory be disentangled from other constituents of highly adverse properties.

The third, and it is considered the most important, reason for the rapidity of adoption of solvent extraction is the intense competition which has been engendered by the belief that the solvent-extracted oils are in themselves superior to products previously obtainable. This in a way is an extension of the second reason, for it merely means that any oil can be improved by extraction. The extent to which it can be treated economically is usually a measure of the proportion extractable. This may vary from some oils where nearly the whole would be dissolved away to others where only 15–20 per cent. reduction below present yields would be experienced. Broadly, too, the better base is likely to make the better finished oil as judged by the evaluating methods at present in use. The differential, however, both in performance and price will not be nearly

so marked as in the past. For this reason it is fairly safe to prophecy that solvent extraction in one form or another will be applied in the not very distant future to all but the lower-grade products. The whole standard of lubricating-oil manufacture will have been raised.

It is for the purpose chiefly of permitting discussion of the claims of solvent extraction to produce high-quality oils of unvarying standard from a wide variety of crudes, and to see how the products behave under present methods of laboratory inspection, that this paper has been written. The process chiefly dealt with is that of propane-cresylic acid extraction. It is not intended in any way to compare or contrast this process with any other. Published results have shown that excellent products may be obtained by the use of a variety of solvents, each process having its own adherents and field of use. It will be as well, however, for the purposes of clarity, rapidly to describe the operation of the propane-cresylic acid process.

It consists of the selective extraction of the oil from its solution in liquid propane by cresylic acid containing a mixture of phenol and cresols in a settled proportion. The extract contains what is generally referred to as the naphthenic fraction of the oil. The propane solution retains that known as the paraffinic. Neither of these terms is likely to be truly descriptive of the chemical nature of the hydrocarbons concerned. It might be better non-committally to describe the extract as consisting of hydrogen-poorer and the residue or raffinate of hydrogen-richer carbon compounds. Certain is it that the extract contains such materials as carbonize more readily, crack to give high octane value motor fuels, and generally behave like hydrocarbons related to the aromatic series. In addition, many of the sulphur compounds are removed together with the gum-forming unsaturated compounds and viscous resins which conventionally have to be destroyed by acid. All of these are less stable than the corresponding bodies left behind. Moreover, they have lower viscosity indices. By virtue of their removal the raffinate is automatically improved in thermal or chemical stability and in viscosity.

The extent to which individual oils are refined is determined not only by their nature, but also by economic exigence. Excessive extraction loss may not be balanced by increased value of the remainder. It is essential, therefore, that the process be flexible. In the case of the process under consideration, this is largely aided by the properties of the propane. Not only does the latter act as a special solvent for the crude stock and raffinate, but its presence greatly increases the specificity of the cresylic acid. In addition, it throws down asphaltic compounds from solution, and in consequence these materials ultimately join the other unstable compounds in the extract.

In practice the operation is carried out as a counter-current procedure, the counter-flow being first established and the stock to be treated introduced at an intermediate point. By suitable establishment of complete equilibrium at chosen points in either direction, it is possible almost completely to prevent loss of good oil in the extract stream, and conversely to adjust the composition of the raffinate stream to any standard required.

The remainder of the process consists essentially of recovery of the solvents. Each layer undergoes a similar treatment, since the separation

of the extraction layers is not complete. The propane is removed in one or more flashes, and the vapour from each layer combined, re-compressed and condensed for further use. The cresylic acid recovery is similarly accomplished, in two towers. The first stage, which removes the bulk of the solvent, is by steam heat at ordinary pressure, and the final stripping accomplished under vacuum with the extract delivered hot by a pipe still and using steam at the base of the tower.

In effect, solvent removal by these means is very complete, but any traces of the cresylic acid which may pass through to the paraffinic raffinate are completely removed in the clay filtration and dewaxing finishing processes.

So much for the process itself. As a refining method its claims are clear and substantiable. It ensures removal of the more unstable compounds without recourse to chemical treatment; it can be applied to a wide range of stocks, and can be varied according to the nature of these raw materials or to the requirements of the products.

Incidentally it is to be observed that solvent extraction limits the applicability of vacuum distillation. The latter process is applied not merely as a method of separating the lubricating oil into fractions according to their boiling points, but also as a means of avoiding thermal decomposition during the separation. This it has successfully accomplished, but might better have left undone in the case of many oils cut thereby out of inferior stocks. Distillation under high vacuum in these cases might result in good colour and low initial carbon residues, but the oils produced are apt still to contain unstable elements—to a greater extent, in fact, than they would have done if produced by harsher means. In use such oils are apt quickly to break down, and to result in increased wear and consumption.

To be able to form any opinion on solvent extraction in relation to the products, it is necessary first to consider the characteristics these should possess. Numerous properties come under consideration in the buying and selling of motor oils, but many of them have little real significance, and at the best are means of identification or broad indications of more important characteristics. Under this heading come specific gravity, volatility, flash point, colour and numerous other qualities. Such may for the present be disregarded. There are others, however, which appear to be markedly indicative of quality as we understand it in motor and aero oils to-day. They certainly have been widely accepted as such both by oil technologists and engineers, and rightly or wrongly these characteristics have been used either alone or in conjunction with practical experience in the choice of oils for particular purposes; and frequently and less logically in the form of individual laboratory tests in the framing of specifications. These two things—property, and the test which attempts to evaluate that property—are frequently mixed up. When there may be legitimate doubt concerning the rôle played by a particular property in the behaviour of an oil in practice, it is clearly most unsatisfactory to use a test which itself may be merely groping towards a representation of that property in the framing of a specification.

Wilson and Keith,[1] in discussing this subject, have placed the important properties of motor oils in four categories :

Low Pour Point.
Low Carbon Forming Tendencies.
High Viscosity Index.
Resistance to Oxidation.

It does not seem possible for the present purpose to improve on this classification.

Pour Point.

This represents the behaviour of the oil under conditions of cold. For motor and aircraft oils it represents the minimum temperature at which the oil will flow to the parts of the engine to be lubricated. There is no particular significance in having an oil of better flowing behaviour under cold conditions than is required to meet the lowest temperature at which the engine may be expected to start. This is very much higher than may be required for certain purposes for industrial oils. Apart from this the property has little import in the present discussion, since dewaxing treatments are operated separately from solvent extraction. It is to be pointed out, however, that they may become more necessary as an auxiliary owing to the tendency of solvent extraction to concentrate the higher setting compounds in the paraffinic fraction.

Viscosity Index.

This expression of viscosity–temperature relationship in terms of paraffinicity has proved of considerable value as a measure of certain desirable features in lubricating oils—particularly in motor oils. The higher the viscosity index the more nearly will the oil fulfil that ideal condition of having a sufficiently low viscosity to meet conditions of severe cold together with high enough viscosity to give good lubrication and low consumption under severe conditions of engine operation. Improvement in the viscosity index of lubricating oil has been sought after in many directions ever since Dean and Davis [2] expounded their system. Already viscosity indices over the sought-for 100 of full Pennsylvanian character are obtainable from mixed base crudes, and although the " ideal " has yet to be reached, it is now necessary to extrapolate far beyond the century mark in order to characterize the full range of oils preparable in one way or another.

The arguments in favour of oils having that flatness of viscosity curve represented by high V.I. are strong. Expressed in one form or another, this characteristic has always represented the conclusions drawn from accumulated practical experience as to the viscosity qualities desirable in an oil. But at the very time that the greatest advances are being made in this direction it is as well to take stock of the position. It may be that the value to be gained from the abnormally high V.I.'s now being sought is exaggerated. Certainly improvement in this direction, however important, must not be at the expense of other properties which make up the good lubricant. It must be remembered that as a *reductio ad absurdam* paraffin wax itself has the highest known viscosity index of any of the viscous hydrocarbons.

Carbon Formation.

Low carbon formation means less carbon deposit in the engine. A cleaner engine in this way means less de-coking and avoidance of an important cause of detonation and pre-ignition. The formation of carbon in the combustion chambers of internal-combustion engines is widely accepted as being governed by the presence of asphaltic or asphalt-forming bodies in the lubricating oil. This is not strictly the case, even with the inclusion of the broad phrase " asphalt-forming," for there are many other secondary reactions which can and do result in ultimate production of carbon or highly carbonaceous material. Nevertheless, the carbonizing qualities of an oil appear to be related, even if they do not run parallel, to their original content of material precipitable by propane, or, for that matter, by other low-boiling hydrocarbons. Advantage of this fact has been taken in the development of several important types of refining process in which propane alone or propane in conjunction with acid is used for the treatment of asphaltic or mixed base crudes.

To what extent laboratory methods of determining carbon residue are actual measures of this joint precipitation–carbonization quality is debatable. The test methods usually applied appear to suffer from inability to distinguish between the carbon formed from asphaltic compounds and that produced as a result of the complicated series of reactions explicable possibly in terms of cracking and re-cracking. Desirability for such differentiation is clear both as means of interpreting the incidence as well as the nature of combustion chamber deposits. At present a good deal is lacking in this respect, for with the increasingly severe conditions met, especially in aircraft engines, higher temperatures alone will alter the course of decomposition of the lubricating oil hydrocarbons caught up in the hot zone. In combination with these heat stresses are the much increased pressures of operation and the increased mechanical effects due to bigger physical dimensions and higher speeds.

It is for this reason that modern laboratory tests like that developed by the Air Ministry are important. Such oxidation tests may be framed to give results in terms of increased viscosity and carbon formation, or in terms of sludge. They definitely represent stability, and thermal stability in the case of hydrocarbons means, amongst other things, minimization of secondary carbon formation and deposit in the engine.

Oxidation and/or Thermal Stability.

The most serious effects of oxidation and thermal instability of lubricating oils are seen in the formation of sludges and in the gumming of piston rings. Sludge deposits somewhat similar to those produced by direct oxidation in the laboratory are liable to be formed in the engine. These are generally produced in crank cases by dispersion of carbon and adventitious solid impurities in partly oxidized oil. When this occurs, oil filters may become choked and feeds blocked up. This cuts off the oil supply to parts of the engine, with resulting damage. Gumming, on the other hand, seems to partake more directly of a thermal nature. If the oil gums, the piston rings are likely to become fouled with resinous material,

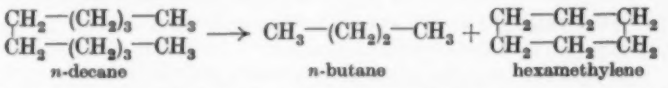
which interferes with their free action and causes high oil consumption. If the process is allowed to continue, valve stems may stick and piston rings set solidly. Under these conditions operating efficiency soon falls, and there is every possibility of severe damage being done to the engine.

Freedom from this trouble is in many ways the most crucial test of a motor oil. Stability under severe conditions of temperature and oxidation is essential if trouble is to be avoided. Any test indicating such stability is of value even if it does not represent a summation of the diverse happenings within the engine. Carbon tests alone are no indication of value, despite the fact that instability leads to ultimate carbon formation. A hard-run engine will to a large extent dispose of its own carbon, but not so the gumming of its piston rings. It is, then, as a measure of stability that such oxidation tests as the Air Ministry test above mentioned are of particular value.

It seems, in point of fact, that outside the combustion chamber heat oxidation may even be secondary to temperature effect. In considering the stability requirements of lubricating oil, the course of decomposition in each case should be given due weight. It is of some importance that both appear to pass through similar if not identical stages towards a common end. This, by the way, is a point practically appreciated by those inventors of the past who endeavoured to use air or oxygen as an adjunct to cracking. There was no appreciable effect on the nature of the products, even of the residues, although such methods were often developed with that end in view.

The heat decomposition of the three chief types of hydrocarbons which may be present in lubricating oils, sometimes doubtless represented in the same molecules, is as follows :

Paraffins.—In this case, the alternative ways of splitting are many, but the first stage of the reaction is preponderatingly the formation of smaller paraffin molecules and olefines. No carbon is formed and no hydrogen liberated. Of special interest in the present connection is the formation of paraffin molecules and naphthenes as first pointed out by Lewes.[3] For example :

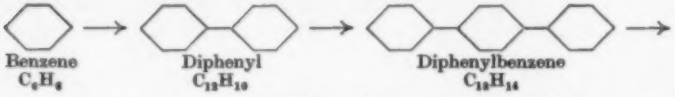


Under the continued influence of heat the olefines endeavour to condense and polymerize to higher-molecular-weight substances progressively poorer in hydrogen. It is in this way, rather than by splitting of the simple molecules, that carbon is ultimately formed.

Naphthenes.—The relative stability of these bodies towards heat depends on the number and nature, *i.e.* the paraffinicity, of the side-chains. They either split the side-chain only, giving low-molecular-weight paraffins and olefines and lower-molecular-weight naphthenes, or dehydrogenate with the formation of aromatics. The unsaturated naphthene nucleus itself tends to condense and polymerize.

Aromatics.—In this case the action is still simpler, since heat merely splits off the side-chains, leaving the unsaturated residue to condense or polymerize to increasingly hydrogen poorer compounds.[4] The actual course

of this action is probably, therefore : Oil hydrocarbons ⟶ Aromatics ⟶ Resins ⟶ Asphaltenes ⟶ Carbenes ⟶ Carboids ⟶ Carbon. In this connection it is to be noted that Sachanen [5] discards the alternative suggested by Zanetti and Egloff [6] as to direct formation of carbon, and gives the following course for its formation from benzene :



Condensation products containing several benzene nuclei ⟶ Carbon

Compare this with the known production of asphaltic bodies by oxidation or sulphurization : Marcusson,[7] whose views are widely accepted on the subject,[8] suggests the origin of asphalt in this way to be the oxidation of cyclic compounds such as naphthenes to polynaphthenic acids (the true asphaltogens), which are gradually turned into anhydrides on heating. These in turn condense to unsaponifiable substances distinguishable by their properties as resins and asphaltenes. Although these bodies are definitely oxygenated or sulphurized, it is to be noted that there is progressive impoverishment in hydrogen and increase in molecular weight in apparently similar manner to the heat reactions.

It is reasonable, from all this, to conclude that increasing the paraffinicity of a hydrocarbon will reduce its potential production of resin, carboids and carbon, whatever the actual temperature and time reaction involved. In the case of lubricating oils the relative chemical difficulty of the paraffins to form the necessary dehydrogenated polymers to produce gum and carbon should unquestionably result in improvement in this direction by specific solvent extraction.

At the same time, it may be concluded that the results of heat–oxidation tests will run parallel to the tendency of an oil to form gum and carbon in the engine. Also that they will come closer together, and the tests give a more direct interpretation of improvement in such qualities the more severe the test conditions as regards time and/or temperature.

It is not possible to fix laboratory heat or oxidation conditions exactly to simulate those in the engine, although it is suggested that heat should play a greater part and air or oxygen a smaller than is generally arranged in such tests. It may be, however, that, as already suggested, the laboratory oxidation merely speeds up the action, and thereby represents the more severe heat conditions in the engine. The following data are of interest in this connection, and should be considered with the foregoing and with the results of laboratory tests and practical experience :

(*a*) The lowest temperature noted at which dehydrogenation of hydrocarbons by means of heat alone occurs is 260° C. (Engler).[9]

(*b*) The time/temperature relationship in cracking is exemplified by the fact that the same result is obtained in 20 seconds at 500° C. as in 49 hours at 275° C.[10]

(*c*) Under normal running conditions the maximum temperatures of the pistons of internal-combustion engine are for aluminium 250° C. and for cast iron 440° C. (Gibson).[11]

(*d*) The conditions of the Air Ministry oxidation test are blowing 40 c.c. of oil with 15 litres of air hourly for two six-hour periods at 200° C.

Results.

Viscosity Index.—Up to the present more attention seems to have been paid to this aspect of the effect of solvent treatment of oils than to any other. Its importance relative to the qualities already discussed is a matter for argument—largely to be influenced, no doubt, by the particular interests of source of production involved. In any case, it is a quality of greater interest in motor oils than aircraft oils. In motor oils the viscosity of the crank-case oil plays a big part in easy starting at low temperatures. At the other end of the scale retention of sufficient body is essential under high-temperature conditions of engine operation and surroundings to ensure good lubrication and low oil consumptions.

By special treatments and choice of raw materials it is possible to make oils of very high viscosity index. Oils of 120 V.I. are by no means laboratory curiosities. It is necessary, however, to hold a careful balance between all the properties desired in an oil and to see that their attainment is kept in perspective with practical value and ultimate cost. For this reason it is of greater interest to observe the effects of solvent refining on individual types of oil than to emphasize the maximum effect which can be produced by its aid. In the following table Oil (A) is prepared by solvent refining from the same Mid-Continent source, and in the same refinery as the Conventionally Refined Oil—a motor oil of normally good class.

Table I.

	Conventional Oil.	Solvent Refined Oil (A).
Viscosity, Saybolt		
100° F.	450″	390″
130° F.	210″	184″
210° F.	61″	59″
Viscosity Index	97	105

An aviation oil prepared by solvent extraction from the same crude oil as (A) gave in comparison with a Pennsylvania aviation oil :

Table II.

	Pennsylvania Oil.	Solvent Refined Oil (D).
Viscosity, Saybolt		
100° F.	1890″	1756″
210° F.	122″	120″
Viscosity Index	90	92

More striking results could be quoted, but the points particularly to be brought into prominence are the way in which solvent treatment has permitted the mixed base crudes to overhaul the Pennsylvanian oils as sources of high V.I. products, and the effect this has had on the nature

of the high-grade motor oils of the world. In this latter connection the following table of viscosity readings of solvent-refined oils side by side with those of their immediate predecessors is significant :

TABLE III.

Grade.	Extreme Winter.		Winter.		Summer.		Aviation.		Heavy Aviation.	
Treatment.	Solv.* (E.)	Conv.† (E′.)	Solv. (F.)	Conv. (F′.)	Solv. (G.)	Conv. (G′.)	Solv. (H.)	Conv. (H′.)	Solv. (I.)	Conv. (I′.)
Viscosity, Redwood										
70° F. .	610″	870″	1315″	1520″	2160″	3147″	3200″	3100″	4400″	5000″
100° F. .	255″	338″	475″	510″	740″	939″	1000″	1000″	1350″	1540″
140° F. .	108″	125″	172″	166″	250″	273″	320″	315″	410″	460″
200° F. .	54″	56″	65″	63″	83″	83″	100″	98″	120″	121″
Viscosity Index . .	117	97	100	84	100	84	110	100	99	94
Specific Gravity .	0·870	0·885	0·880	0·900	0·885	0·905	0·882	0·890	0·888	0·895

Even more striking is the way in which the solvent-refined oils traverse the present S.A.E. classification. Fig. 1 shows the viscosity–temperature curve of a standard solvent-treated light motor oil superimposed upon the curves for average S.A.E. grades, from S.A.E. 10-W, the lightest recognized grade to S.A.E. 30, a distinctly summer grade. The solvent oil is the equivalent in viscosity of an average S.A.E. 30 at 250° F., a temperature of some significance in the normal running of an automobile engine. At the other end of the scale, around zero, it is the equivalent of an S.A.E. 20-W grade, and actually approaches the S.A.E. 10-W grade at lower temperatures.

Carbon Residue.—Here again the importance to be ascribed to the results of the test as determined on untreated oil is largely a matter of opinion. Its variation in extent in oils of similar source is, however, of definite significance. The following, taken from a large number of similar results, is of interest as representing exactly similar oils from the same Mid-Continent crude oil and from the same refinery. The third for comparison is a conventionally refined Pennsylvania Oil :

TABLE IV.

	Pennsylvania Oil.	Conventional Mid-Continent Oil.	Solvent-Refined Oil (A).
Specific Gravity . .	0·8861	0·9000	0·8794
Flash Point, open . .	425° F.	415° F.	410° F.
Viscosity, Redwood . .			
100° F. . .	365″	382″	331″
140° F. . .	137″	140″	128″
200° F. . .	57″	57″	55″
Carbon Residue (Conradson) . .	0·53	0·46	0·19
Neutralization Value .	0·05	0·03	0·01

* Solvent refined. † Conventionally refined.

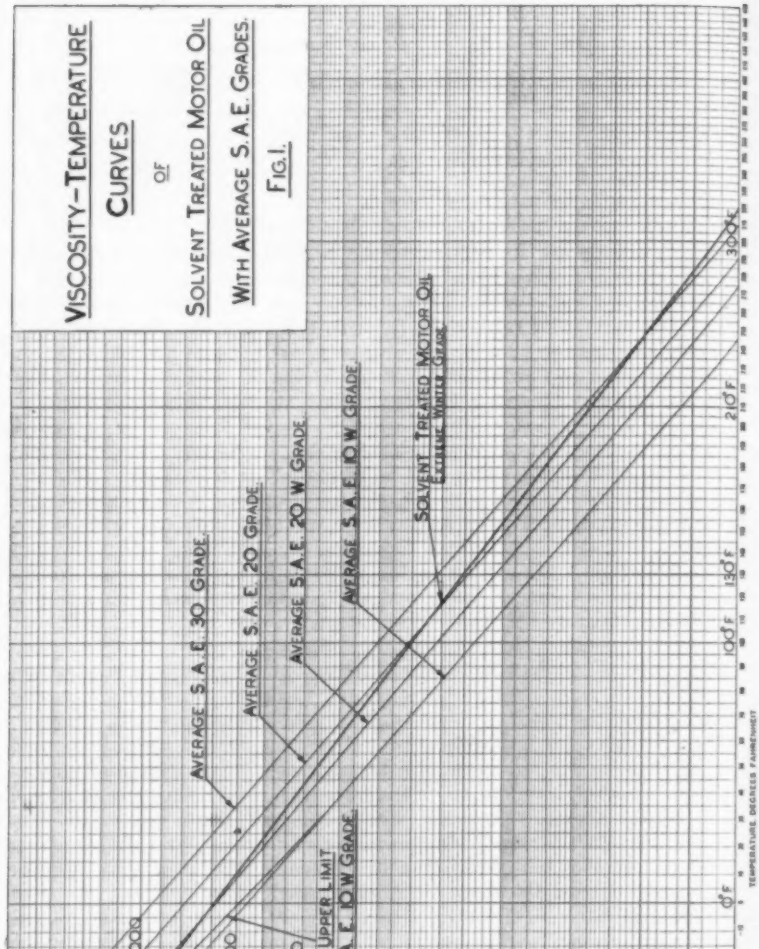
Similar pairs of tests (Ramsbottom) on solvent-refined motor oil (B) and solvent-refined aircraft oil (C and D) with their exactly corresponding conventionally refined oils are of interest :

TABLE V.

	Carbon Residue.
Solvent Refined (B)	0·28
Conventionally Refined Mid-Continent	0·80
Solvent Refined (C) Aviation	0·29
Conventionally Refined Pennsylvania	0·88
Solvent Refined (D) Aviation	0·34
Conventionally Refined Pennsylvania	0·55

These readings are all on commercial products, and are not specially chosen. This course has been followed throughout with all data quoted.

Resistance to Oxidation and Heat.—At the risk of repetition, it must be stated that everything appears to point to this being the most important property of a motor oil. It has always been felt that oxidation is an important factor in the behaviour of crank-case oil, and this, indeed, has been the genesis of most laboratory oxidation tests for lubricating oils. It has not been agreed, however, what effects are liable to be produced on the oil by heat and oxidation, either in the laboratory or in the engine, nor the counter-effects which will be produced on the engine. Barnard and co-workers of the Standard Oil Company of Indiana [12] have endeavoured to correlate oxidizability, or at any rate chemical stability, with sludge formation; sludge, in turn, with formation of asphaltenes, and both with engine condition. Disastrous as the wide variety of crank-case sludges can be in the clogging of filters and the possible engine failure resulting therefrom, it seems likely that these sludges are only partly and indirectly oxidation products. Most of them are largely composed of adventitious matter, metals and metallic oxides, carbon from the under side of piston heads, carbon from blow-past and so on, dispersed by means of partly oxidized oil as the peptizing agent in the remaining unchanged oil. Indeed, if there is anything in Nellensteyn's [13] asphalt theory conditions seem almost ideal for the formation of carbon oleosols. But with stuck piston rings the situation is different. Here, for a start, is an occurrence of known effect on the engine. Moreover, it is a snowball effect, due to the fact that with stuck-fast rings piston temperatures increase, and the gumming therefore becomes progressively more severe. This is a great danger throughout the whole range of internal-combustion engines. It is of especial importance in high-duty aircraft engines, where overheated pistons are particularly likely to cause trouble. Two-stroke engines also are very prone to piston-ring trouble, because of the hot combustion gases impinging directly on the top rings when the exhaust port is uncovered. All of these facts seem to support the theoretical conclusions previously reached that heat, possibly even more than oxidation, is responsible for the decomposition of the lubricating oil into the resinous materials which gradually form in piston-ring grooves, and which there may eventually bake or coke solidly. At any rate, the actual temperatures involved are high, so that resistance to heat in an oil becomes proportionately more important.


VISCOSITY–TEMPERATURE
CURVES
OF
SOLVENT TREATED MOTOR OIL
WITH AVERAGE S.A.E. GRADES.
FIG. I.
AVERAGE S.A.E. 30 GRADE.
AVERAGE S.A.E. 20 GRADE.
AVERAGE S.A.E. 20 W GRADE
AVERAGE S.A.E. 10 W GRADE
SOLVENT TREATED MOTOR OIL
EXTRA WHITE GRADE
UPPER LIMIT
S.A.E. 10 W GRADE
200,000
10,000
2000
500
200
100
60
40
0°F
100°F
130°F
210°F
300°F
VISCOSITY SAYBOLT UNIVERSAL SECONDS
TEMPERATURE, DEGREES FAHRENHEIT

Since the development of the British Air Ministry oxidation test other tests have come into being along the same lines. It is a pity that with such comparatively new tests standardization could not have been effected. Here is a comparison of the three tests with which the author has been chiefly concerned—the Air Ministry,[14] the Indiana [15] and the Socony : [16]

TABLE VI.

Oxidation Test.	Quantity of Oil.	Quantity of Air.	Temp.	Observations.
British Air Ministry	40 c.c.	15 l./hr.	392° F.	Increase in viscosity and carbon residue after two 6-hour periods.
Indiana	300 c.c	10 l./hr.	341° F.	Times required to form 10 mg. and 100 mg. asphaltenes per 10 gr. oil. Viscosity increase every 50 hours. Up to 150/200 hours.
Socony	300 gr.	2 l./hr. with stirring.	350° F.	Sludge as asphaltenes × 10 every 24 hours for 7 days or until 15% sludge is formed. Viscosity, carbon residue, N.V. and evaporation loss on completion of test.

No attempt has been made to correlate these tests, nor is there any need to do so, except that it might be possible thereby to learn which is the most discriminating as regards stability. On the face of it the Indiana and Socony tests, with their longer times and lower temperatures of treatment, appear more " descriptive " of motor conditions and the Air Ministry test of aviation conditions.

In view, however, of the importance of piston-ring fouling in general and its apparent dependence on heat, the Air Ministry test has much to commend it for general acceptance. Moreover, the shorter time involved makes it more practical. As a result, the suggestion has been welcomed that the temperature of oxidation might be still further increased, and opportunity has been taken of examining the behaviour of conventionally-and solvent-refined oils under progressive rise of temperature, other conditions of operation remaining the same. The results, as shown in the following tables and in Figs. 2, 3, 4, 5 and 6, are very striking. The difference in viscosity increase with rise of temperature over 220° C. is particularly marked. This feature presumably represents the formation of oil-soluble oxidation or polymerization products of the asphalteneogen or resinous type, since at identical temperatures the solvent-treated oils give nil asphaltene values. This freedom from asphalt formation is maintained at still higher temperatures than those quoted.

These results not only speak of the great stability of the solvent refined oils; they also indicate that for the best discrimination between oils as regards stability, the test adopted should be operated at as exalted a temperature as is compatible with practical convenience and repeatability. Since the higher temperatures also represent more nearly the conditions met in practice, the reframing of heat tests along these lines should be given sympathetic consideration.

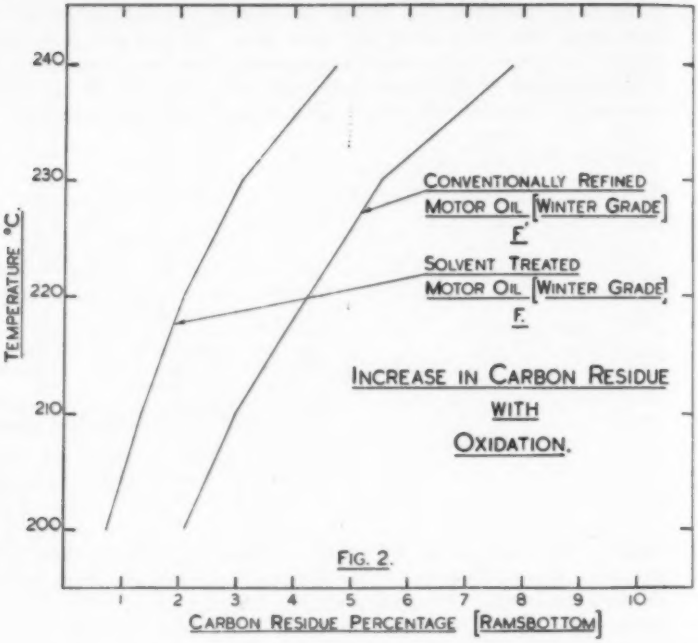

240
230
220
210
200
TEMPERATURE °C.
CONVENTIONALLY REFINED
MOTOR OIL [WINTER GRADE]
E.
SOLVENT TREATED
MOTOR OIL [WINTER GRADE]
F.
INCREASE IN CARBON RESIDUE
WITH
OXIDATION.
1 2 3 4 5 6 7 8 9 10
CARBON RESIDUE PERCENTAGE [RAMSBOTTOM]

FIG. 2.

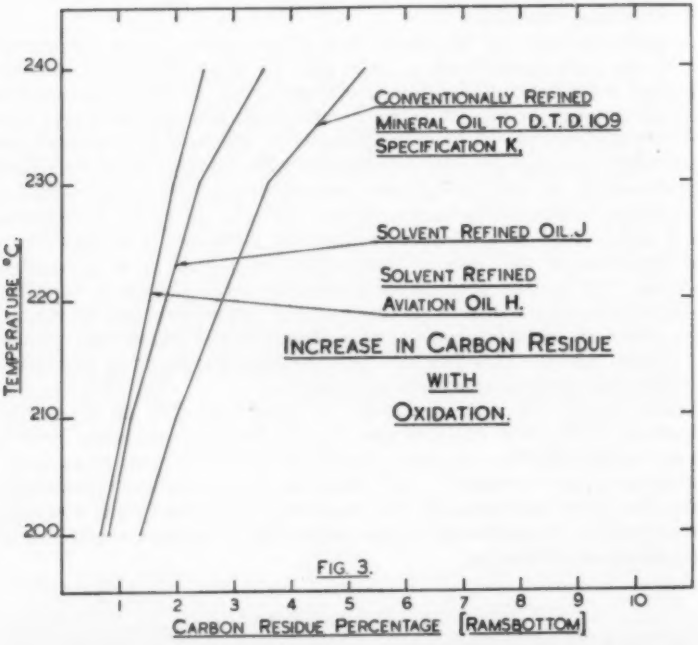

240
230
220
210
200
TEMPERATURE °C.
CONVENTIONALLY REFINED
MINERAL OIL TO D.T.D. 109
SPECIFICATION K,
SOLVENT REFINED OIL J.
SOLVENT REFINED
AVIATION OIL H.
INCREASE IN CARBON RESIDUE
WITH
OXIDATION.
1 2 3 4 5 6 7 8 9 10
CARBON RESIDUE PERCENTAGE [RAMSBOTTOM]

FIG. 3.

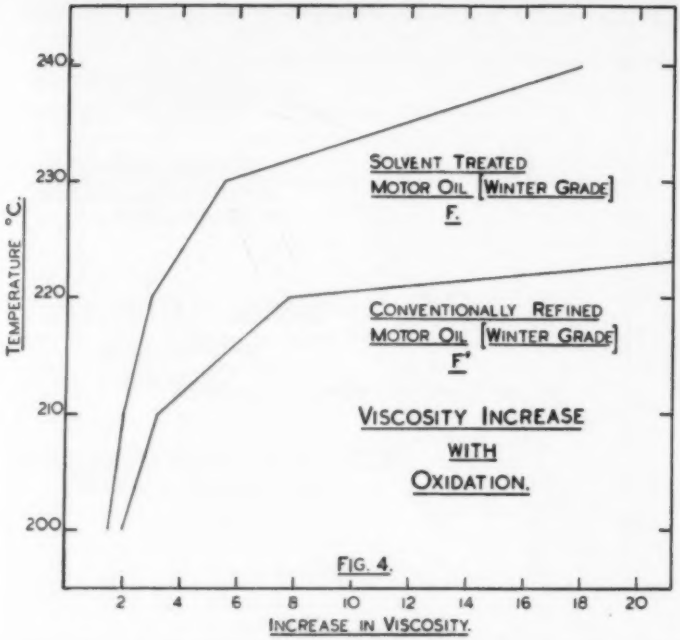

240
230
220
210
200
TEMPERATURE °C.
SOLVENT TREATED MOTOR OIL [WINTER GRADE] F.
CONVENTIONALLY REFINED MOTOR OIL [WINTER GRADE] F'
VISCOSITY INCREASE WITH OXIDATION.
2 4 6 8 10 12 14 16 18 20
INCREASE IN VISCOSITY.

FIG. 4.

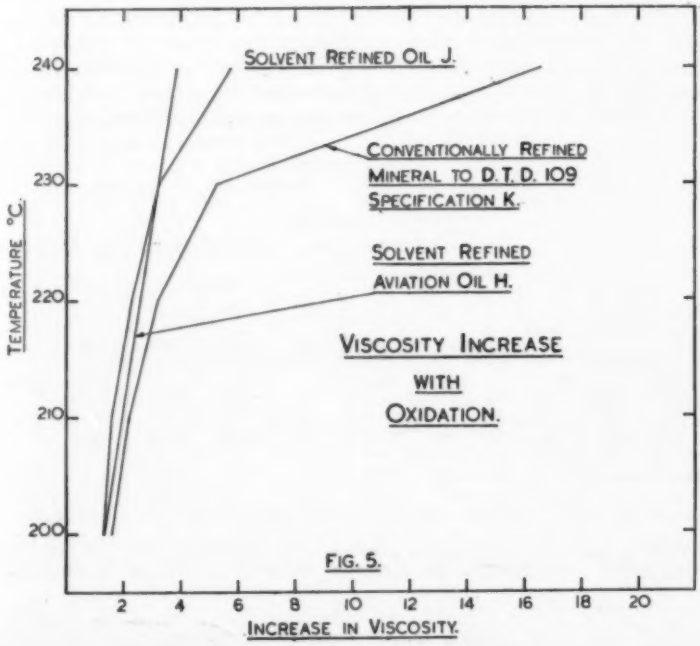

240
230
220
210
200
TEMPERATURE °C.
SOLVENT REFINED OIL J.
CONVENTIONALLY REFINED MINERAL TO D.T.D. 109 SPECIFICATION K.
SOLVENT REFINED AVIATION OIL H.
VISCOSITY INCREASE WITH OXIDATION.
2 4 6 8 10 12 14 16 18 20
INCREASE IN VISCOSITY.

FIG. 5.

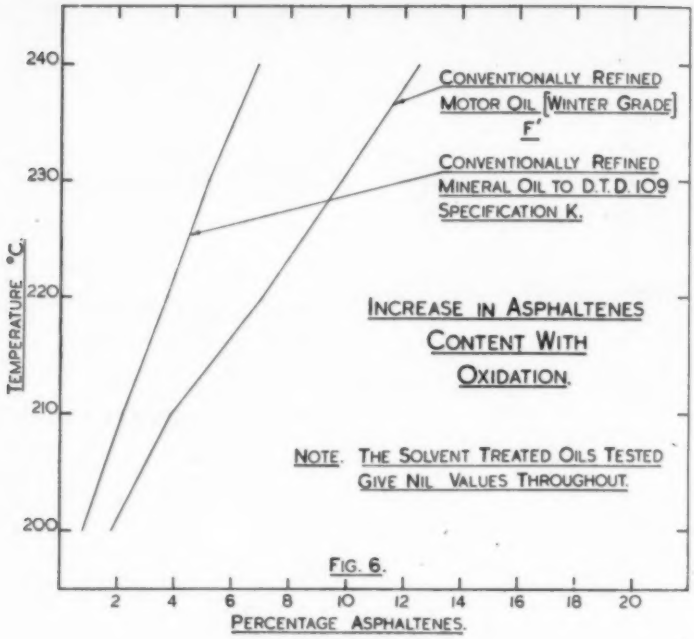

240
230
220
210
200
TEMPERATURE °C.
CONVENTIONALLY REFINED MOTOR OIL [WINTER GRADE] F'
CONVENTIONALLY REFINED MINERAL OIL TO D.T.D. 109 SPECIFICATION K.
INCREASE IN ASPHALTENES CONTENT WITH OXIDATION.
NOTE. THE SOLVENT TREATED OILS TESTED GIVE NIL VALUES THROUGHOUT.
2 4 6 8 10 12 14 16 18 20
PERCENTAGE ASPHALTENES.

FIG. 6.

TABLE VII.

Oil.	Carbon Residue (Ramsbottom) with Rise of Temperature.						
	Before Oxidation.	Temperature of Oxidation.					
		200° C.	210° C.	220° C.	230° C.	240° C.	250° C.
Solvent-refined Motor Oil (F) . .	0·25	0·74	1·37	2·09	3·10	4·75	—
Conventionally-refined Motor Oil (F') . .	0·58	2·08	3·00	4·23	5·53	7·87	—
Solvent-refined Aviation Oil (H) .	0·22	0·68	—	—	1·99	2·50	2·98
Solvent-refined Aviation Oil to average DTD 109 viscosity (J)	0·31	0·77	1·20	1·82	2·40	3·52	—
Average DTD 109 Specification Oil (naphthenic base) (K)	0·47	1·35	2·0	2·79	3·57	5·10	—
	0·47	1·40	—	—	3·32	4·75	5·58

Oil (J) is chosen as having almost identical mean viscosity figures to Oil (K). The solvent-refined aviation oil (H) also conforms, of course, to DTD 109 specification.

TABLE VIII

Oil.	Increased Viscosity at 100° F. with Rise of Temperature.				
	Temperature of Oxidation.				
	200° C.	210° C.	220° C.	230° C.	240° C.
F . .	1·44	2·02	2·78	5·45	18·0
F′ . .	1·97	3·18	7·76	66·0	—
H . .	1·38	—	—	—	3·84
J . .	1·28	1·60	2·23	3·07	5·78
K . .	1·60	2·04	3·15	5·37	17·0

TABLE IX.

Oil.	Asphaltene Formation with Rise of Temperature.					
	Before Oxidation.	Temperature of Oxidation.				
		200° C.	210° C.	220° C.	230° C.	240° C.
F . .	Nil	Nil	Nil	Nil	Nil	Nil
F′ . .	Nil	1·74	3·90	7·06	9·80	12·50
J . .	Nil	Nil	Nil	Nil	Nil	Nil
K . .	Nil	0·75	2·20	3·76	5·20	6·90

To cross-check these conclusions, tests were made with the oils referred to in Table IX, modifying the conditions to the low temperature of 150° C., but increasing the time to a maximum of 75 hours (Table X). The difference between the solvent-treated and the conventionally-treated oils is still clear, but for discriminatory purposes the alterations and rates of alteration are immaterial in comparison with the results obtained by increase of temperature.

TABLE X.

Oil.	Oxidation at 150° C.									
	Carbon Residue.				Increased Viscosity at 100° F.			Asphaltenes.		
	Before Oxidation.	25 hours.	50 hours.	75 hours.	25 hours.	50 hours.	75 hours.	25 hours.	50 hours.	75 hours.
F .	0·25	0·31	0·33	0·38	1·06	1·11	1·13	Nil	Nil	Nil
F′ .	0·58	0·67	0·75	0·85	1·08	1·16	1·19	Nil	Nil	0·05
J .	0·31	0·33	0·37	0·41	1·04	1·08	1·10	Nil	Nil	Nil
K .	0·47	0·55	0·62	0·70	1·09	1·12	1·17	Nil	0·01	0·23

Mechanical Tests.—So far the solvent-refined oils have been discussed only as regards their physical characteristics in the unused state or their chemical stability when subjected to heat and oxidation. Mechanical

tests intended to be indicative of the behaviour of lubricating oils in practice have many limitations, and except in certain special cases are not yet recognized as of importance in determining lubricating value. It is evident, however, that such tests may be used for supplying information of considerable interest. This is especially so in the present case, where it may legitimately be queried whether the method of refining under review in developing certain desirable features in lubricating oils has done so at the expense of others—notably film strength and lubricity.

A number of machines have been devised from time to time to observe the behaviour of oil and to measure its coefficient of friction under

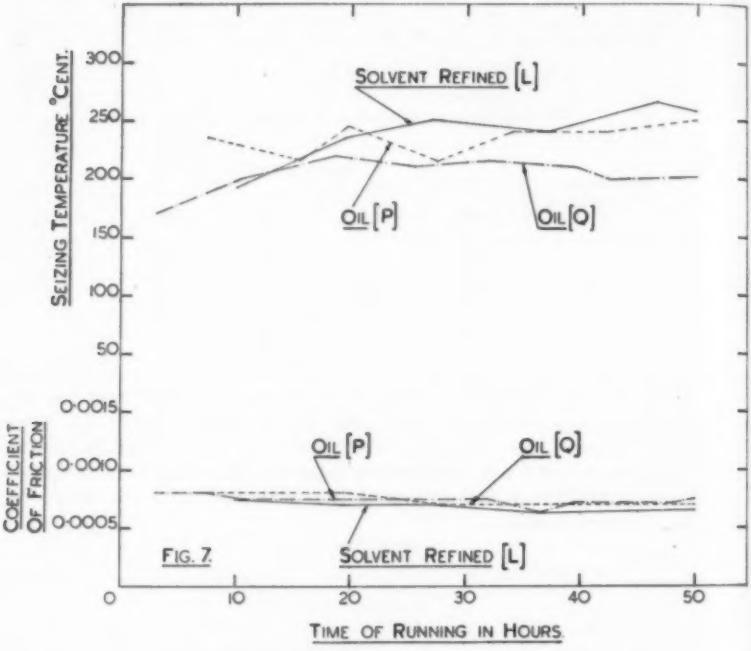


FIG. 7.

given conditions. One of the most interesting is that developed at the National Physical Laboratory. This machine has been used for a large number of tests, mostly in connection with investigations on oils for internal-combustion engines. A high degree of repeatability can be obtained by a skilled operator. The machine and its method of use are very similar to that described at an earlier Meeting of the Institution by R. O. King.[17]

The method of test may be summarized as follows :

The oil is fed by a circulating pump to a bronze bearing accurately machined to give an oil space of 0·002 in. around a steel shaft 2¼-in. diameter. The bearing carries a load equivalent to 1000 lb./sq. in., and the shaft is driven at 1300 r.p.m. Means are provided for measuring

accurately the temperature of the bearing and the frictional drag between the bearing and shaft. The temperature of the bearing, and therefore of the lubricating oil in it, can be varied by control of a gas burner heating the steel shaft. On its return from the bearing to the reservoir, the oil has hot air at 160° C. blown into it.

The normal test is for 50 hours in daily periods. After starting, the bearing temperature rises and the coefficient of friction falls, due to reduction of viscosity of the oil. A temperature is reached at which the coefficient of friction has a minimum value, and most of the run is made in this state. Towards the end of each daily run the bearing temperature

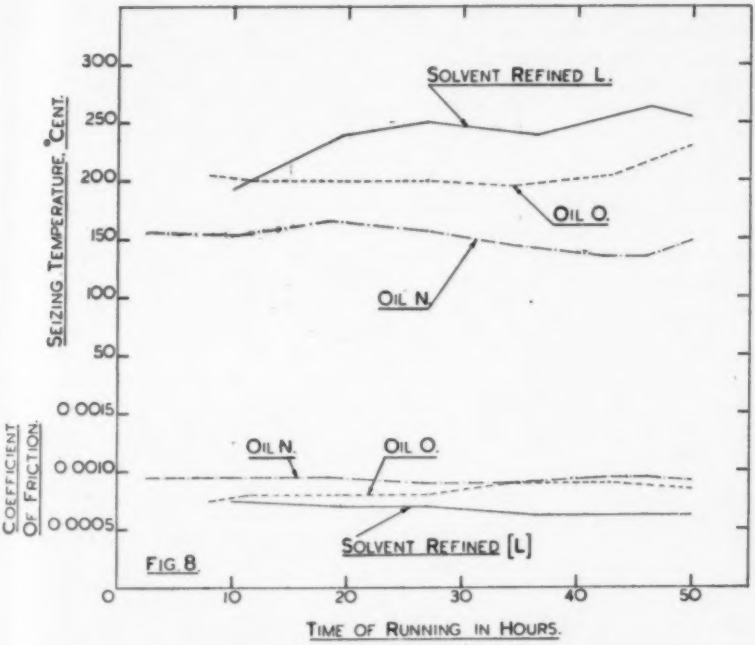


FIG. 8.

is increased, and eventually the coefficient of friction reaches such a value that the bearing seizes and throws off the driving-belt. This temperature is termed the Seizing Temperature. No damage is done to the bearing surfaces, and after the machine has cooled overnight, the test is repeated.

The results are generally shown graphically (*a*) as the variation of coefficient of friction with bearing temperature; (*b*) as Seizing Temperature plotted to a base of time of running; and (*c*) as "Minimum Coefficient of Friction" to the same base.

The results of comparative tests of solvent-refined oils and others of similar viscosity, but conventional refining, are shown in Table XI and Figs. 7 and 8.

The curves of most of the conventionally refined oils indicate an increase

in seizing temperature and a decrease in coefficient of friction as the test progresses, but the solvent-refined oils show less variation. This is to be expected from their chemical stability. It is quite remarkable, however, that their S.T. is consistently higher and their coefficient of friction lower than in ordinarily refined oils.

What these tests mean it is difficult exactly to gauge. High S.T. almost certainly represents ability of an oil to withstand a high SPEED × LOAD factor, and provide a margin of working safety.

In any case, it is quite clear that oils do not suffer in this respect or as regards their coefficients of friction by reason of their being solvent refined. The contrary, indeed, is the case.

Engine Tests.—Laboratory tests, whether physical, chemical or mechanical, are attempts to reproduce artificially some of the things that an engine does to the oil when it is in use. The most important consideration to the user, however, is what the oil does to the engine; and whilst it may be possible to deduce this with some accuracy from the laboratory tests, none has yet been devised which can take the place of a test in an engine.

In modern high performance engines, of which aircraft engines are perhaps the best examples, piston and piston ring lubrication is, as already implied, the most important and difficult problem of lubrication. Here engine tests are of especial value in showing the actual behaviour of an oil in fouling the rings, grooves and piston skirts.

TABLE XI.

	Solvent Refined.		Conventionally Refined.			Conventionally Refined and Compounded
	(L)	(M)	(N)	(O)	(P)	(Q)
Specific Gravity	0·883	0·883	0·897	0·924	0·910	0·904
Viscosity, Redwood						
70° F.	2220″	2650″	2500″	3418″	2725″	2350″
100° F.	784″	930″	837″	987″	785″	753″
140° F.	260″	311″	257″	272″	233″	240″
200° F.	83″	99·4″	83″	79″	70″	76″
Viscosity Index	97	110	90	62	59	88
Seizing Temperature mean (approx.)	240° C.	235° C.	155° C.	205° C.*	210° C.	230° C.
Minimum Coefficient of Friction, mean	0·00067	0·00070	0·00095	0·00080	0·00075	0·00075
Oxidation Test						
Carbon Residue						
before	0·31	—	0·43	0·69	—	—
after	0·88	—	1·37	3·40	—	—
Viscosity Increase	1·31	—	1·50	3·48	—	—

* Intermittent seizures at lower temperatures.

Tests on complete aircraft engines are extremely costly, particularly as they must be of considerable duration if conclusive results are to be obtained. It is customary, therefore, to make such tests in special single-cylinder test engines, where strictly comparative results can be obtained.

FIG. 10.

PISTON. SINGLE-CYLINDER GLYCOL-COOLED TEST ENGINE. CONVENTIONALLY-REFINED COMPOUNDED AIRCRAFT ENGINE OIL. 100 HOURS TEST.

FIG. 9.

PISTON. SINGLE-CYLINDER GLYCOL-COOLED TEST ENGINE. CONVENTIONALLY-REFINED HIGH-QUALITY AIRCRAFT ENGINE OIL. 100 HOURS TEST.

[*To face p.* 76.

FIG. 11.

PISTONS. SINGLE-CYLINDER GLYCOL-COOLED TEST ENGINE. SOLVENT-REFINED AIRCRAFT ENGINE OIL. 100 HOURS TEST.

In addition, such tests can frequently be accelerated to give results in a shorter time, and whilst such results may not be strictly parallel to actual practice, they are still found to give accurate comparisons between different oils.

One method of accelerating such tests is to use glycol cooling for the cylinder jackets in place of the customary water cooling. Air cooling is more difficult to use in test work of this nature, on account of the greater number of variables involved. Illustrations are given of the results of such tests in Figs. 9, 10 and 11.

From the photographs of pistons given it will be seen that ordinary high-quality oils give practically complete failure in 100 hours' run, due to sticking of the piston rings in their grooves. Similar tests using a suitable solvent-refined oil show the piston rings to be perfectly free and the deposits very greatly reduced. In fact, the piston is fit for further use without cleaning.

Admittedly, results such as these would not occur in less than, say, 500 hours' flying at high speed, possibly very much longer. They are comparable, however, and by showing the great improvement that can be effected in practice with solvent-refined oils, accord with the results obtained by chemical and mechanical tests.

The author wishes to express his thanks to his colleagues of the Vacuum Oil Co., Ltd., and in particular to Messrs. Day and Gullick and Dr. Harris, for their assistance in the preparation of this paper.

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[3] *J.I.P.T.*, 1914–15, **1**, 167.
[4] Cf. *Berl. Petr. Z.*, 1930, **26**, 1027.
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SOLVENT EXTRACTION PROCESSES.*

By W. R. Wiggins, B.Sc., and F. C. Hall, M.Sc., A.I.C. (Student Member).

The introduction of solvent refining methods in lubricating oil manufacture is due primarily to developments in the automobile and aircraft industries. The increasing efficiency of internal-combustion engines with concurrent increase in bearing pressures, speeds and temperatures, calls for lubricating oils of particularly high resistance to sludging, low pour point, low viscosity change with temperature, and minimum carbon deposition in service. Oils produced by conventional refining methods from available crudes are not wholly satisfactory in all such factors, and blending effects no more than a compromise. Especially does this apply to oils of pronounced naphthenic type, such as those of Gulf Coast and Californian origin, which exhibit low oxidation resistance and low viscosity indices.

By solvent refining, it is possible to produce from widely differing lubricating oil stocks, oils having viscosity indices and oxidation stability equivalent to, or exceeding, those of Pennsylvanian origin, whilst retaining the low carbon-forming characteristics of naphthene base distillates. Such results are, in general, unobtainable by conventional acid refining, or alternatively involve heavy refining losses and difficulties in treatment.

Solvent extraction separates to a varying degree the high- and low-grade components of a lubricating stock, and cannot, therefore, produce more high-grade oil from it than is present in the original stock. In the case of extremely naphthenic oils, the yield of high-grade material is naturally low, but by reason of the flexibility of the process, the yield from a stock can be increased to any required extent at the expense of the quality. The degree of separation to be effected will obviously depend on the type of stock treated and the economic considerations governing the balance between the yield and quality of the finished oil. The low-grade components separated are available for cracking stock or in certain cases for the production of asphalt.

Selective Extraction with Solvents.

The hydrocarbons present in lubricating oil stocks may, for practical purposes, be divided into two classes: "paraffinic" constituents of predominantly open-chain structure and "naphthenic" components which appear to be essentially cyclic compounds of high carbon–hydrogen ratio. Although not precise, these terms serve to differentiate between those constituents of lubricating oils having satisfactory physical and chemical properties, such as high viscosity index, low viscosity–gravity constant, and high oxidation stability, and the naphthenic constituents which are inferior in these respects. Distillation processes effect separation of

* Paper presented for discussion at the One Hundred and Sixty-eighth Meeting of the Institution of Petroleum Technologists, December 10th, 1935.

hydrocarbons on the basis of boiling point, or molecular weight, and do not otherwise differentiate between chemical classes. Such separation may be effected by solvent extraction processes.

Selective solvents used in extraction processes are compounds which when mixed with the lubricating stock at a suitable temperature form two liquid phases. The naphthenic constituents are invariably more soluble, and hence are concentrated in the solvent phase, whilst the less soluble paraffinic compounds, with dissolved solvent, form the second phase. In selective extraction the solvent and lubricating stock are mixed under conditions ensuring efficient solvent–oil contact. The two phases are allowed to separate, are withdrawn, and the solvent is removed by distillation, or other means. The oil obtained from the solvent phase is termed the extract, and that from the hydrocarbon phase is known as the raffinate.

The chief properties necessary for a commercial selective solvent are as follows :—

1. Chemical stability; the solvent must be stable in storage and under operating conditions, and must not react chemically with the oil processed.
2. Good selectivity; the solvent must be capable of effecting a sharp separation between the paraffinic and naphthenic constituents.
3. Adequate solvent power; the solvent should be capable of dissolving a reasonable amount of naphthenic oil. The solvent power may be increased by raising the extraction temperature, but this is only effected at the expense of selectivity.
4. The two phases formed must be capable of sharp separation, this being facilitated by a reasonable gravity differential between the solvent and stock treated.
5. The solvent should be easily and completely recoverable from the raffinate and extract phases, this being effected, in practice, by distillation.

Other factors of importance in plant design include specific heat, latent heat, vapour pressure, flash point, toxicity and corrosive power. Low specific and latent heats reduce the heat required for solvent removal. Low vapour pressure reduces evaporation loss, high flash point minimizes fire hazards, non-toxicity involves less risk to personnel,[1] and the solvent should be non-corrosive under the conditions of operation.

In Table I some of the more important physical properties of solvents which have been used in large-scale plant operation are summarized.

The solvent–oil ratio used in extraction processes is largely dependent on the selectivity and solvent power of the solvent; the selectivity diminishes with increasing temperature, whilst the solvent power increases. For a given solvent and extraction system the solvent–oil ratio will vary according to the type of oil processed and the yield and characteristics of the raffinate required.

The method of extraction used influences the efficiency of the process, and thus the amount of solvent necessary. The highest efficiency is offered by multiple-stage counter-current or packed tower continuous counter-current extraction.

TABLE I.

Solvent.	Sp. Gr.	M. P. °F.	B. P. °F.	Solubility in Water.	Flash Point. °F.	Remarks.
Sulphur dioxide	1·43	−105	14	23 per cent. at 32°	—	Suffocating gas, corrosive in presence of water
Benzole . .	0·88	42	175·5	0·02 per cent. at 32° F.	—	Inflammable, 90 per cent. grade used
Nitrobenzene .	1·21	47·7	412	0·2 per cent.	208	Toxic, non-corrosive
Phenol . .	1·07	109	361	10·5 per cent. at 100° F.	—	Toxic
Cresylic acid .	1·04	below −100	365–400	Less soluble than phenol	—	—
Chlorex . .	1·22	− 61	352	1 per cent. at 68°	168	Fairly low toxicity
Furfural . .	1·16	− 34	323	5·8 per cent. at 96°	138	Low toxicity
Crotonaldehyde	0·86	−101	215	Slightly soluble	—	Oxidizes readily
Acrolein . .	0·84	−125	126	—	—	Toxic
Propane . .	0·54 (at 32° F.)	—	−49	—	—	—

The maximum temperature which can be employed in extraction is limited by the fact that complete miscibility of solvent and oil is possible, in the majority of cases, at a sufficiently high temperature. For efficient extraction the temperature employed must be such as to secure a satisfactory balance between selectivity and solvent power. It is dependent on both the solvent used and the stock treated, paraffin base residuals requiring a higher temperature than naphthenic distillate stocks. Whereas moderate temperatures reduce heat requirements, higher temperatures enable viscous stocks to be handled with ease.

Distillate stocks are most readily treated by solvent extraction, residual oils, particularly those of asphaltic character, offering greater difficulties. Residual stocks are more efficiently dealt with by selective solvents of high solvent power.

The raffinate obtained from a given stock in general exhibits lower specific gravity, viscosity–gravity constant, and viscosity, with higher viscosity index, reduced carbon residue and considerably improved oxidation resistance. The colour is improved, with resultant reduction in the finishing treatment required for marketable products, whilst in the case of sulphur-containing stocks the sulphur content is considerably reduced.

The characteristics of the raffinate obtained will be determined by the efficiency of extraction, but more particularly by the type of stock treated and the raffinate yield. The quality of the raffinate is improved in inverse proportion to the yield obtained.

The use of wax-bearing stocks does not affect solvent extraction, but since the wax (of extreme paraffinic nature) is concentrated in the raffinate, and asphaltic constituents are removed in the extract, the pour point of the raffinate is higher than that of the original oil. Although the raffinates

so obtained are in general more readily dewaxed than the original stock, against this must be set the factor that dewaxing losses on the raffinate are of far greater economic importance than in the case of the untreated oil.

Many solvents have been investigated for the selective extraction of lubricating oil stocks, but only a limited number have been utilized in commercial processes. The more important of these are discussed in the following section.

Sulphur Dioxide Treatment.

The application of liquid sulphur dioxide as a solvent refining agent originated in the Edeleanu process for the removal of aromatic, unsaturated and sulphur-containing constituents of kerosine. A natural development followed in the utilization of this process for light lubricating oils.

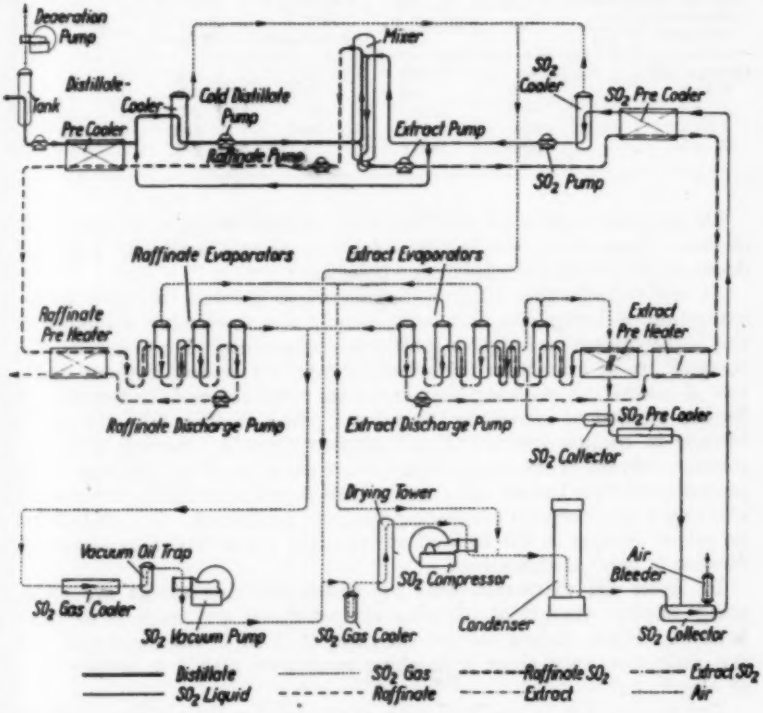


Fig. 1.

Flow diagram of liquid SO_2 process.

The essential features of operation with distillates are as follows[2]: the charging stock, after passage through pre-coolers, is chilled to the operating temperature by injection of liquid sulphur dioxide. The oil is then pumped into the lower part of the contact mixing tower through which

it rises, coming into counter-current contact with liquid sulphur dioxide. The sulphur dioxide–extract layer is continuously drawn off from the bottom of the tower; the raffinate leaving the tower near the top. Both extract and raffinate, after passage through the charging stock pre-coolers, are freed from sulphur dioxide by multi-stage evaporation, at increasing temperature and decreasing pressure. Operating costs for the treatment of kerosine and light oils by this process have been estimated to be of the order of 8 to 10 cents per barrel of stock treated.[3]

The improvement in characteristics of a light spindle oil, using various solvent–oil ratios, is shown in Table II.[4]

TABLE II.

Solvent/Oil Ratio. [Extraction temperature 14° F.]	Yield %.	Sp. Gr. 60/60° F.	Viscosity at 100° F. Centistokes.	Carbon Residue Conradson.	Sligh Oxidation Number.
Original oil . .	—	0·899	41	0·13	60
0·5 : 1 . .	88·6	0·884	36·5	0·04	35
1 : 1 . .	85·6	0·880	35	0·03	29
1·5 : 1 . .	83·0	0·877	34·5	0·03	22
2 : 1 . .	80·9	0·876	34	0·02	14

The sulphur content of the raffinate is considerably lower than that of the original stock, but further solvent treatment results in a smaller decrease of the residual sulphur compounds.

At low temperatures sulphur dioxide shows reduced efficiency in the extraction of heavy oils, this being largely due to the low solubility of the higher-molecular-weight naphthenic components. By increasing the temperature of extraction the solvent power is increased without undue loss of selectivity, enabling heavier stocks to be successfully treated. A further method of increasing the solvent power is offered by the use of benzole in conjunction with liquid sulphur dioxide. Benzole is a non-selective solvent of extremely high solvent power, and by variation in the proportions of the two solvents used, a high degree of flexibility is obtained, allowing a wide range of lubricating stocks to be treated. It is stated that no major changes in the method of operation are involved by the introduction of these modifications.

In Table III extraction data for widely differing stocks are given, using sulphur dioxide at differing temperatures, and sulphur dioxide–benzole. In all cases a solvent–oil ratio of 2 to 1 was employed, and the raffinates were given a finishing treatment with 3 to 20 per cent. of clay.[5]

The process can be modified with advantage for the refining of stocks yielding low percentages of high-grade raffinates, by carrying out the extraction in two stages. The stock is first treated with sulphur dioxide alone to give a fairly high yield of raffinate. The latter is then further extracted with sulphur dioxide–benzole. The final raffinate is a high-grade lubricating oil, whilst the sulphur dioxide–benzole extract fulfils the requirements of a low grade motor oil or industrial lubricant.

TABLE III.

Charging Stock.	Treatment.	Extraction Temp. ° F.	Yield % by Vol.	Sp. Gr. 60/60 ° F.	Viscosity Centistokes.			Viscosity Index.	Viscosity–Gravity Constant.	Conradson Carbon Residue.	Colour N.P.A.
					100° F.	130° F.	210° F.				
Californian	—	—	—	0·964	567	—	16·8	−80	0·910	0·51	Dark Green
,, SO_2		25	65	0·927	255	—	13·9	16	0·864	0·16	3½
,, SO_2		95	51	0·921	230	—	13·8	31	0·856	0·11	3½
,, SO_2-Benzole (85 : 15)		25	54·8	0·919	214	—	13·2	33	0·855	0·06	2½
,, SO_2-Benzole (75 : 25)		25	47·8	0·914	200	—	13·0	38	0·847	0·05	1½
East Texas	—	—	—	0·915	131	—	11·2	64	0·853	0·53	Dark
,, SO_2		113	73·6	0·887	77·5	—	9·1	86	0·819	0·06	2½
,, SO_2-Benzole (75 : 25)		30	73·1	0·885	72·5	—	9·1	96	0·817	0·04	2
Mid-Continent	—	—	—	0·898	62	—	7·8	86	0·842	0·18	—
,, SO_2		25	88·7	0·881	51·5	—	7·4	99	0·823	0·07	3
,, SO_2-Benzole (85 : 15)		32	82·9	0·876	49	—	7·3	101	0·816	0·06	2½
Mid-Continent	—	—	—	0·924	—	294	36·6	69	0·843	3·06	Dark Green
,, SO_2-Benzole (60 : 40)		32	70·4	0·893	—	138	24·4	95	0·808	0·56	5½
,, SO_2-Benzole (50 : 50)		32	62·0	0·889	—	133	24·0	97	0·804	0·46	5
Mid-Continent (Residual)	—	—	—	0·927	—	248	34·2	78	0·847	4·7	Dark
,, SO_2-Benzole (50 : 50)		32	69·6	0·891	—	104	21·4	105	0·808	0·72	7
Mixed Base	—	—	—	0·969	—	760	58	27	0·90	7·3	—
,, SO_2-Benzole (75 : 25)		14	68·7	0·917	513	186	28·9	89	0·84	1·2	—

Table IV illustrates this process applied to a propane-treated Kettleman Hills long residuum.[6]

TABLE IV.

Treatment.	Product.	Yield % by Vol. of Original Stock.	Sp. Gr. 60/60° F.	Viscosity in Centistokes. 210° F.	Viscosity Index.	Viscosity-Gravity Constant.
200 per cent. sulphur dioxide at 115° F.	Original	—	0·940	20	30	0·874
Raffinate from above treated with 250 per cent. by vol. SO_2–benzole (70 : 30) at 90° F.	First Extract	24	1·000	28	—	0·950
	Second Extract	44·4	0·939	20	39	0·874
	Final Raffinate	31·6	0·897	18	90	0·820

The processing costs for sulphur dioxide–benzole treatment of Mid-Continent cylinder stock have been estimated at approximately 17 cents per barrel of charge for a 2000-barrel plant; for the two-stage process treating Californian distillate the corresponding cost for a 1500-barrel plant is given as 21 to 22 cents per barrel.[7]

PHENOL PROCESS.

The original commercial plant using phenol has been in operation since 1930, and other plants have been installed subsequently. The operation

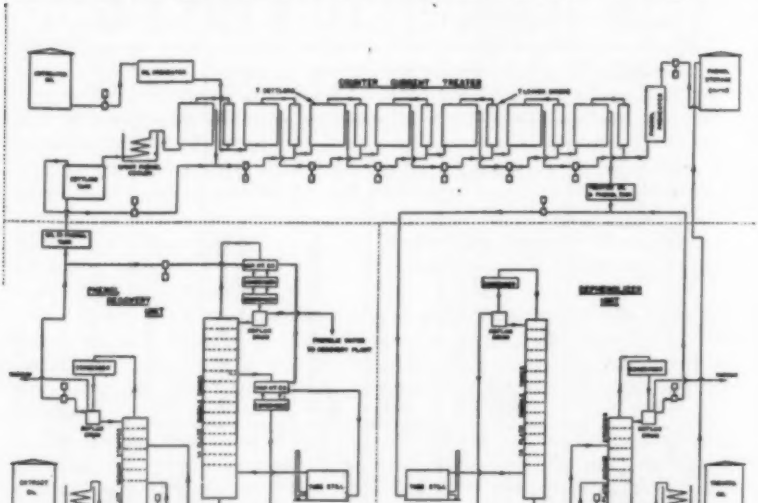


FIG. 2.

FLOW DIAGRAM OF PHENOL PROCESS.

of the plant consists essentially of counterflow mixing of oil and solvent through a series of seven (Leaver) mixers and corresponding settling tanks. The stock and solvent are pre-heated separately to 110–125° F., and entering at opposite ends of the seven-stage extractor come into countercurrent contact, a solvent–oil ratio of 125 to 165 per cent. of phenol being used for Colom biandistillates. Treated oil, containing 8 to 15 per cent. phenol, from the final settling tank, is pumped to a pipe still from which the heated oil passes to a bubble tower, where the phenol is distilled. The residual oil finally passes through a vacuum stripper, where the

TABLE V.

Stock.	Treatment.	Yield %.	Sp. Gr. 60/60° F.	Viscosity 210° F. Centistokes.	Viscosity Index.	Viscosity–Gravity Constant.	Pour Point.
Light Colombian	Countercurrent, 125 per cent. solvent at 120° F.						
Original .		—	0·924	12·0	40	0·862	— 5
Raffinate.		60	0·888	10·3	85	0·817	— 5
Extract .		40	0·983	20·5	—	0·930	40
Heavy Colombian	Countercurrent, 125 per cent. solvent at 120° F.						
Original .		—	0·932	18·9	23	0·864	5
Raffinate.		61·8	0·896	14·5	79	0·823	15
Extract .		38·2	0·997	49·2	—	0·937	55
Extra Heavy Colombian	Countercurrent, 165 per cent. solvent at 125° F.						
Original .		—	0·950	31·0	28	0·880	30
Raffinate.		53·3	0·900	20·5	77	0·822	45
Extract .		46·7	1·001	114	—	0·930	95

separation is completed; the quantity of phenol remaining in the treated oil being of the extremely low order of 0·005 per cent. The solvent phase, which is discharged from the first settling drum, after passage through the contact unit, is cooled and passed to a settling tank maintained at 95–100° F. The oil separating from the cooled solvent phase is recycled through the extraction unit, and the solvent, which contains 25–30 per cent. of oil, then passes through a phenol recovery unit similar to that used for separating the phenol from the raffinate. The extract oil has a phenol content of less than 0·07 per cent.

The flexibility inherent in the phenol process enables a wide range of lubricating fractions to be handled, from low viscosity transformer and

turbine oils to heavy cylinder stocks. These raffinates usually require a clay contact only as finishing treatment. Refining data for commercial treatment of Colombian distillates are listed in Table V.[8, 9]

Operating costs, exclusive of labour and fixed charges, based on a charge of 1200 barrels per day, are stated to be about 14·5 cents per barrel of charging stock, or 24–29 cents approximately per barrel of raffinate. Labour costs are low, since only a small personnel is required for plant operation. Solvent losses for a period of three years on the plant described amounted to about 0·15 per cent., and have been reduced to 0·1 per cent.;

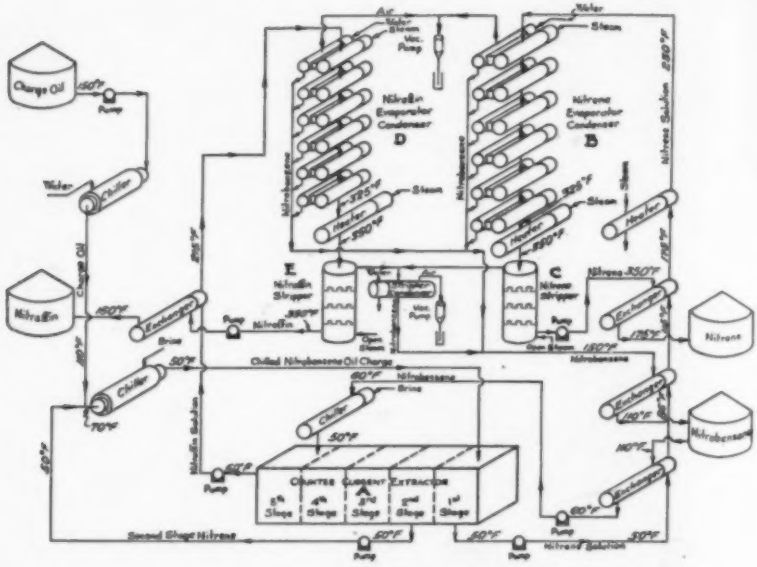


FIG. 3.

FLOW DIAGRAM OF NITROBENZENE PROCESS.

corrosion occurring in the phenol recovery unit has been found to be due to the sulphides and organic acids concentrated in the extract, and this difficulty has been eliminated.

THE NITROBENZENE PROCESS.

Research by Ferris and others[10] of the Atlantic Refining Co., on a large number of solvents, showed that nitrobenzene possesses to a high degree the properties necessary for selective extraction of lubricating oil stocks. This solvent combines good selectivity with high solvent power, whilst its high specific gravity facilitates separation of the two phases. Nitrobenzene is applicable both to residual and distillate stocks, ranging in character from extremely naphthenic to Pennsylvanian.

In this process[11] extraction is carried out in a conventional five-stage

counter-current extractor consisting of five rectangular settlers, each of which provides one hour of settling, with inter-stage mixers. The extraction temperatures are adjusted to suit the character of the charging stock, varying from about 30° F. for naphthenic oils to 120° F. approximately for highly paraffinic oils. The charge oil, after preliminary chilling, is mixed with the nitrobenzene phase from the second stage of the extractor. After further chilling to the operating temperature, the mixture enters the first stage of the extractor and proceeds through the stages in counter-current flow to fresh nitrobenzene entering at the fifth stage. The final raffinate and extract phases from the extractor are passed through cascade-type vacuum evaporators, working down to a final pressure of 10 to 50 mm. and a maximum temperature of 325° F. Final traces of the solvent—1 to 2 per cent.—are removed by stripping with live steam at 350° F. under vacuum. A temperature limit of about 350° F. is desirable to avoid oxidation of the oil by nitrobenzene, which takes place at higher temperatures.

Inspection data for results with different charging stocks are given in Table VI.[12]

TABLE VI.

Oil.	Viscosity at 210° F. Centistokes.	Viscosity–Gravity Constant.	Viscosity Index.	Carbon Residue.
Mid-Continent distillate				
Original	12·7	0·852	83	0·46
Raffinate	12·2	0·811	102	0·11
Coastal distillate				
Original	16·6	0·850	47	0·53
Raffinate	17·0	0·803	89	0·07
Coastal distillate (140% solvent; 50–77° F.; 3-stage yield 52%)				
Original	28·9	0·859	—	—
Raffinate	19·5	0·816	—	—
Extract	53	0·897	—	—
Coastal Residuum				
Original	34·2	0·863	—	1·0
Raffinate	32·3	0·830	—	0·5

Dewaxing is preferably carried out on the treated oil (raffinate) rather than on the charging stock. The reduction in colour through nitrobenzene extraction usually eliminates the necessity for acid treatment, a finishing treatment with clay being sufficient.

The solvent loss in this process is stated [13] to be of the order of 0·08 per cent., while operating costs have been estimated to be 30 to 37 cents per barrel of charge.

CHLOREX.

Chlorex (ββ′-dichloroethyl ether) has been developed as a selective solvent for refining lubricating oil stocks by the Standard Oil Co. of Indiana.[14] In addition to its high degree of selectivity, the solvent power

of Chlorex is sufficiently high to enable heavy residuum stock to be handled, whilst the low viscosity and high specific gravity facilitate separation of the two extraction phases.

Table VII illustrates the selectivity of Chlorex in comparison with nitrobenzene, the stock being extracted with 200 per cent. of solvent at a temperature 43° F. below that of miscibility.

TABLE VII.

Oil.	Yield.	Sp. Gr.	Viscosity at 210° F. Centistokes.	Viscosity Index.	Viscosity–Gravity Constant.	Extraction Temp. °F.
Original.	—	0·897	7·1	78	0·845	—
Chlorex raffinate	74·8	0·884	7·1	104	0·828	77
Nitrobenzene raffinate	51·1	0·877	6·9	104	0·819	50

Industrial units for extraction with Chlorex have been constructed with varying types of extraction and solvent recovery systems. It is considered that four-stage counter-current extraction is adequate to deal with para-

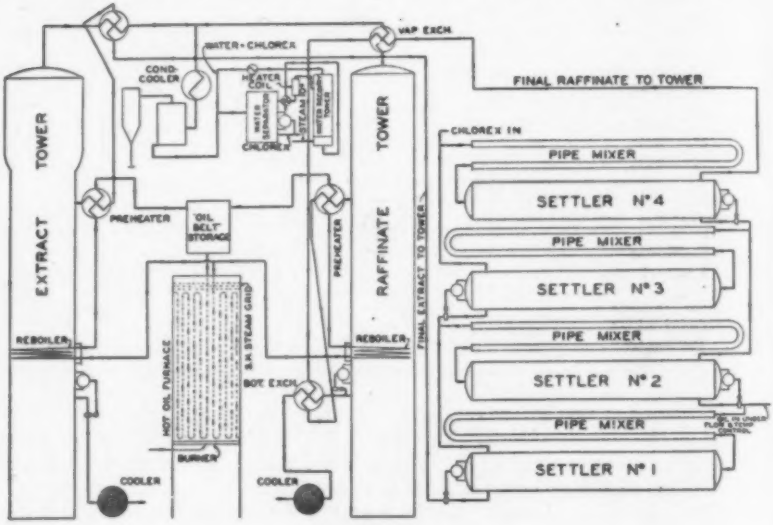
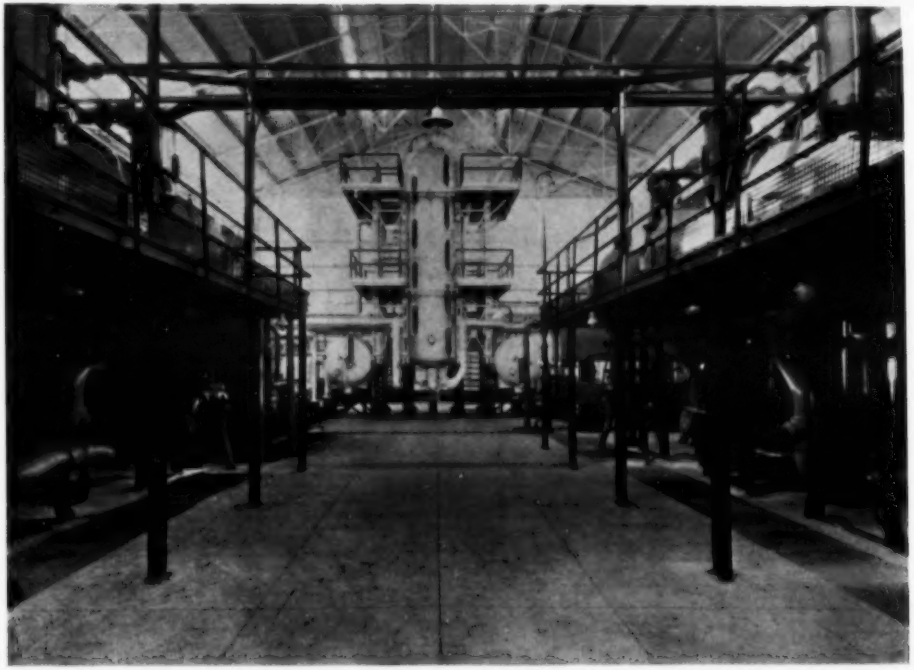


FIG. 4.

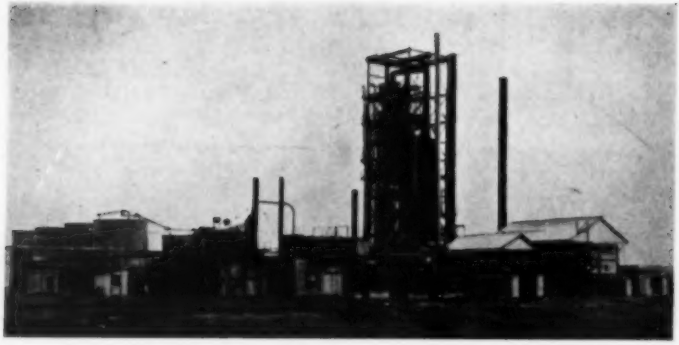
FLOW DIAGRAM OF CHLOREX PROCESS.

ffinic stocks, but up to seven stages have been used with Coastal oils. The following details relate to a unit recently constructed in Pennsylvania, utilizing four stages, and processing 500 barrels of neutrals per day.[15] The stock, raised to the extraction temperature (60–125° F., depending on the characteristics of the stock) is fed to the first-stage pipe mixer with the

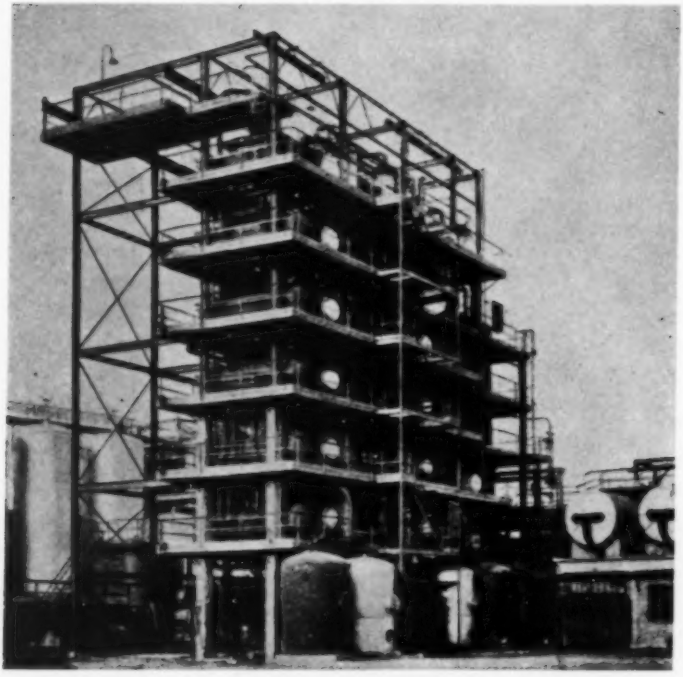


EDELEANU PLANT, SHOWING RAFFINATE EVAPORATORS AT THE LEFT AND EXTRACT EVAPORATORS AT THE RIGHT. IN THE CENTRE IS THE MIXER, TO THE LEFT OF WHICH IS THE RAFFINATE COLLECTOR AND TO THE RIGHT THE EXTRACT COLLECTOR.

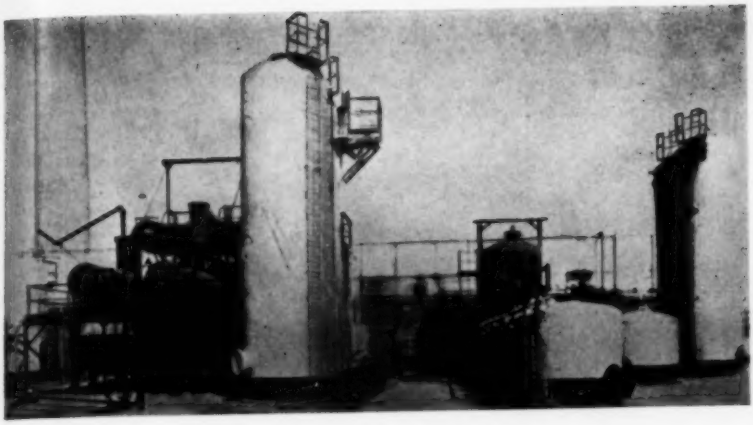
[*To face p.* 88.



GENERAL VIEW OF PHENOL PLANT.

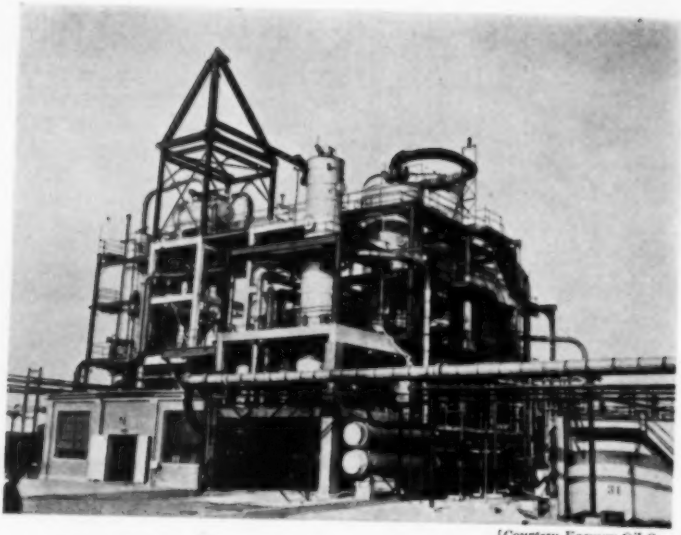


GENERAL VIEW OF NITROBENZENE PLANT.



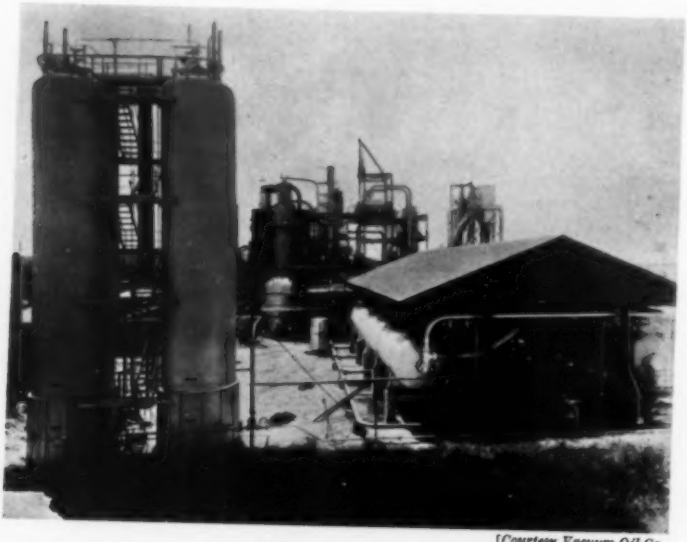
GENERAL VIEW OF CHLOREX PLANT.

GENERAL VIEW OF FURFURAL PLANT.



[*Courtesy Vacuum Oil Co.*

DUO-SOL PLANT, SHOWING TOWERS, EXCHANGERS AND CONDENSERS.



[*Courtesy Vacuum Oil Co.*

DUO-SOL PLANT PROPANE TOWERS IN FOREGROUND, EXTRACTION SHED ON RIGHT AND SOLVENT RECOVERY SYSTEM BEHIND.

Chlorex extract from the second stage, and thence to the first settling tank. From this the extract layer is pumped to a stripping tower, whilst the raffinate phase passes through the remaining extraction stages in counter-current flow to fresh Chlorex entering at the last stage. The final raffinate and extract phases are pumped to their respective solvent recovery towers, via heat exchangers, where the charge is flashed at 300–320° F. The towers operate at a vacuum of 26–28 inches of mercury and live steam is introduced to assist stripping. The condensed water and solvent are separated by gravity, dissolved Chlorex being recovered from the water by flash distillation. The solvent losses are stated to have been reduced to less than 0·04 per cent. of the Chlorex circulated. The chlorine content of the oils produced does not exceed 0·0017 per cent. for the raffinate, and 0·010 per cent. for the extract, and this is completely eliminated upon clay treatment.

The Chlorex requirements for a plant processing 40,000 gallons of oil per day are of the order of 10,000 gallons,[16] whilst the operating costs for the treatment of Penna oils have been estimated at 17–20 cents per barrel of oil charged.[17]

Typical extraction data for different stocks are illustrated in Table VIII.

TABLE VIII.

Oil.	Viscosity at 210° F. Centistokes.	Viscosity Index.	Carbon Residue.	Sludging Time in Hours.*	Yield %.
Californian	10·0	54	0·64	10	—
Raffinate using 600 per cent. of Chlorex	—	95	0·27	83	—
Mid-Continent	18·2	75	0·78	37	—
Raffinate using 250 per cent. of Chlorex	—	85	0·21	107	—
Pennsylvanian cylinder stock (residuum)	34·7	109	2·07	—	—
After conventional refining	34·4	106	1·44	—	—
After Chlorex extraction and finishing treatment	32·5	109	0·91	—	93 (raffinate)

* Indiana oxidation test: over 70 hours represents very satisfactory resistance to oxidation.

The finishing treatment normally includes dewaxing, if necessary, followed by clay treatment.

FURFURAL PROCESS.

Furfural, as a selective solvent, has been introduced by the Texas Oil Company, and a commercial unit utilizing this solvent has been in operation since 1933. This compound, which can be produced in large quantities from cereal waste, has good selectivity, and is used at relatively high temperatures, enabling viscous distillate and residual stocks to be processed. The high specific gravity of furfural facilitates phase separation, whilst evaporation losses are minimized by its low vapour pressure.

It is further characterized by low toxicity. Although somewhat liable to oxidation, this can be avoided by operation in a closed system.

As in most solvent processes, the continuous counter-current system is used for extraction; in this case a single packed contact tower is employed in place of multi-stage operation.[18, 19] The charging stock is fed through a steam heater to the bottom of the contact tower, the temperature ranging from about 130° F. for low-viscosity or naphthenic oils to 220° F. for high-viscosity paraffinic oils. The furfural is charged through a heat exchanger and steam heater to the top of the tower at temperatures ranging from 160° to 280° F., a temperature gradient being maintained. This tower is packed with about 20 ft. of Raschig rings, with a re-distribution

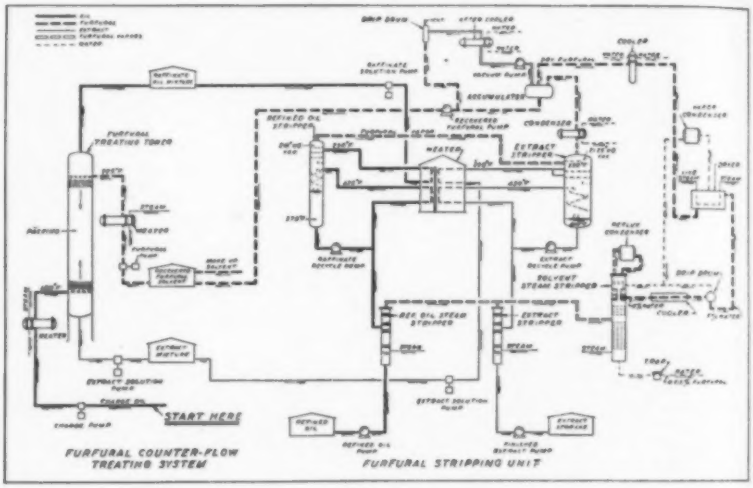


FIG. 5.

FLOW DIAGRAM OF FURFURAL PROCESS.

device for every 4 ft. of packing. External cooling of the extract phase and recycling of the cooled mixture through the lower section of the tower improve fractionation and yields. The raffinate phase, withdrawn from the top of the tower, is separated from the solvent by flash distillation under vacuum and the remaining solvent, amounting to 0·4 per cent., is removed by vacuum steam stripping. The solvent is recovered from the extract phase in three stages utilizing atmospheric distillation, vacuum distillation, and finally steam stripping under vacuum.

Analytical data for typical charging stocks are shown in Table IX.[19]

The finishing treatment adopted usually comprises a light acid treatment followed by a contact clay filtration and final dewaxing. The initial acid treatment may, however, be omitted.

Solvent losses have been reduced to 0·025 per cent. of the total furfural used, while operating costs for Mid-Continent distillates are estimated at 17 to 18 cents per barrel of charge.

TABLE IX.

	Treatment.	Yield. % by Vol.	Specific Gravity. 60/60° F.	Viscosity at 210° F. Centistokes.	Viscosity Index.	Viscosity-Gravity Constant.	Carbon Residue. %.	Pour Point. ° F.
Gulf Coast Distillate—								
Original	—	—	0·941	16·2	−10	0·881	0·14	−5
Raffinate	206 per cent. furfural at 195° to 175° F.	63·3	0·910	13·0	40	0·842	0·04	0
Extract		36·7	0·996	32·5	—	0·942	—	—
Mid-Continent Distillate—								
Original	—	—	0·915	17·4	64	0·844	1·40	110
Raffinate	190 per cent. furfural at 235° to 212° F.	72·5	0·884	13·5	97	0·808	0·14	115
Extract		27·5	0·995	53·9	—	0·933	—	—
Pennsylvania Steam-Refined Residuum—								
Original	—	—	0·904	34·9	105	0·818	3·06	35
Raffinate	276 per cent. furfural at 249° to 232° F.	84·2	0·888	31·4	113	0·799	1·41	—
Extract		15·8	0·985	—	—	—	—	—

TABLE X.

Oil.	Yield. %.	Solvent. %.	Temp. of Treatment. ° F.	Specific Gravity. 60/60° F.	Viscosity at 210° F. Centistokes.	Viscosity–Gravity Constant.	Viscosity Index.	Carbon Residue. %.
Pennsylvania Residuum—								
Original . . .	—	—	—	0·909	49·7	0·820	96	—
Raffinate . . .	89·5	—	—	0·898	44·6	0·807	107	—
Mid-Continent Reduced Pressed Distillate—								
Original . . .	—	120	65–70	0·903	7·2	0·844	66	0·3
Raffinate . . .	81	—	—	0·874	6·8	0·809	96	0·025
California Distillate—								
Original . . .	—	300	60	0·954	13·0	0·900	−34	—
Raffinate . . .	50	—	—	0·912	11·1	0·848	43	—

Crotonaldehyde Process.

A solvent extraction process utilizing crotonaldehyde has been developed by the Foster Wheeler Corporation. This compound is characterized by good solvent power, and the comparatively low boiling point facilitates solvent recovery. The low specific gravity results in a small gravity differential between the phases, and in practice separation is effected by centrifugal means. The related compound, acrolein, of lower boiling point, has also been utilized in this process.

The raw stock and solvent, at 60–90° F. are contacted in a two-stage counter-current extraction system utilizing centrifuges for separation of the phases. The extract and raffinate phases are passed through heaters

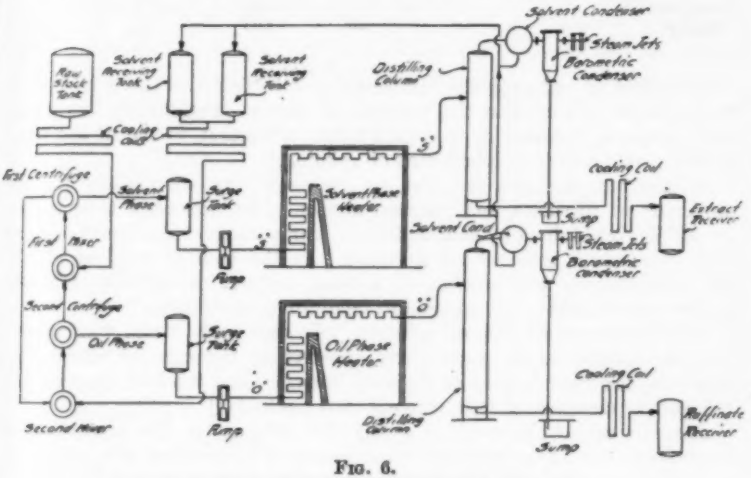


Fig. 6.

FLOW DIAGRAM OF CROTONALDEHYDE PROCESS.

to fractionation towers, where recovery of the solvent is effected. The reduction in time of separation through the use of centrifuges greatly reduces the solvent requirements of the plant. It is probable that centrifugal separation will be more widely adopted in solvent extraction plants in the future.

Process data for Californian and Mid-Continent distillate stocks and a Pennsylvanian residuum are given in Table X.[20]

Use of Liquid Propane.

Brief attention may be given to the application of liquid propane in refining practice.

The tendency of low-boiling paraffins to precipitate out asphaltic material from lubricating oil stocks is particularly pronounced in the case of liquid propane. Addition of liquid propane at ordinary temperatures, under pressure, to an asphaltic residual stock, causes separation into two phases when the propane exceeds a certain critical amount. The asphalt, with

some oil, is precipitated as a heavy viscous liquid; increase in the propane-oil ratio is, up to a point, accompanied by more complete separation of the asphalt, with a corresponding increase in melting point. Beyond this point, no improvement in asphalt separation is observed. The figures in Table XI illustrate the propane de-asphaltization of topped Poso Creek residuum using 10 volumes of liquid propane at 80° F.[21]

TABLE XI.

	Yield. %.	Sp. Gr.	Viscosity at 210° F. Centistokes.	Melting Point. ° F.
Extracted oil	75	0·949	19·1	—
Asphalt	25	1·063	—	176

The effect of reducing the temperature is to decrease the solubility of the asphaltic material in the propane–oil phase. Preliminary treatment with propane, followed by normal solvent extraction, is one of the more recent developments in lubricating oil refining.[22]

At low temperatures propane can be used very successfully for the dewaxing of distillate and residual stocks. The necessary temperature (— 40° F.) is obtained by evaporation of a proportion of the liquid propane with consequent internal refrigeration. In the case of residual stocks, the simultaneous precipitation of a small amount of asphaltic material is not objectionable, and appears to facilitate cold settling.

Acid treatment in propane solution, following asphalt and wax separation, is claimed to be particularly effective in the case of mixed base residuals, the yield of finished oil being increased and the acid consumption reduced, in comparison with conventional methods.[21]

Propane cannot be used as a selective solvent for the separation of naphthenic from the paraffinic constituents of lubricating oils, except in so far as the segregation of paraffin wax and asphaltic material may be considered under this heading, but some degree of fractionation according to molecular weight, as in fractional distillation, can be effected for residual stocks.[23]

DUO-SOL PROCESS.

Although propane is not a suitable solvent for the separation of the paraffinic and naphthenic components, its use in conjunction with a selective solvent, with which it is immiscible, has advantageous features. The presence of a large proportion of propane diluent diminishes the amount of the paraffinic constituents of the oil in the extract phase, and at the same time decreases the solubility of asphaltic and colour bodies in the raffinate phase; under these conditions the extract layer appears capable of dissolving the asphaltic material rejected by the propane.

The use of propane as a secondary solvent has been adopted with marked success in the Duo-Sol process, in which cresylic acid is employed as the selective solvent.[24] This process has a high degree of flexibility, and has been applied with success to the treatment of asphaltic residual stocks. The raffinates obtained have low carbon residue values and show

marked reduction in colour, with consequent elimination of acid treatment and decrease in the amount of clay used for finishing. In the case of highly sulphurous stocks the process is claimed to effect considerable reduction of sulphur content. Selection of the correct solvent–oil and propane–cresylic acid ratios for any given stock is important. Increased amounts of propane improve the colour and yield of the raffinate, but affect adversely the viscosity index and viscosity–gravity constant. The process has been used principally for the treatment of long residual oils, the products being dewaxed and vacuum distilled to yield a range of refined lubricants.

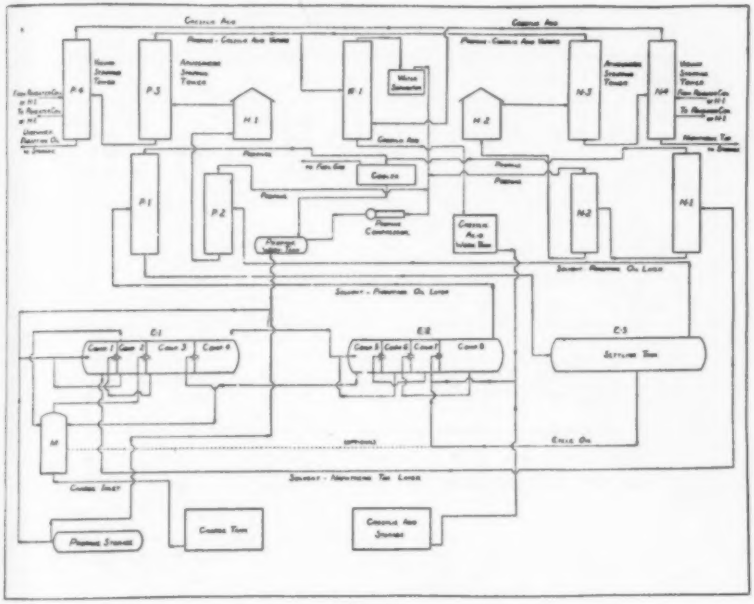


FIG. 7.

FLOW DIAGRAM OF DUO-SOL PROCESS.

The charging stock is contacted with the solvents in two horizontal tanks with eight compartments; the stock enters the No. 3 compartment, cresylic acid enters at No. 8, and liquid propane is introduced at No. 1. The horizontal position of the tanks offers large settling areas, and individual pumps for each compartment cause the solvents to flow counter-currently. The propane raffinate layer leaves at No. 8 compartment, and the extract phase emerges at No. 1. The operations for solvent recovery differ for the extract and raffinate phases because of the difference in boiling points of the two solvents. The extract phase, for a typical run, contains about 20 per cent. propane, 74 per cent. cresylic acid and 6 per cent. of naphthenic compounds. Both phases are passed through heat exchangers, raised to a maximum temperature of 260° F., then delivered to towers working at 190 lb. per sq. in. pressure,

TABLE XII.

Oil.	Cresylic Acid. %.	Propane. %.	Yield. %.	Specific Gravity. 60/60° F.	Viscosity at 210° F. Centistokes.	Viscosity–Gravity Constant.	Colour. N.P.A.	Viscosity Index of Dewaxed Raffinate.	Carbon Residue of Dewaxed Raffinate.
Penna Long Residuum—									
Charging Stock	400	300	—	0·884	13·0	0·808	—	—	—
Raffinate	—	—	92	0·871	10·7	0·795	7½	108	0·38
Extract	—	—	8	1·027	—	—	—	—	—
Iraq Residuum—									
Charging Stock	300	400	—	0·967	42·0	0·899	—	—	—
Raffinate	—	—	55	0·881	8·3	0·813	3½	100	0·17
Extract	—	—	45	1·073	—	—	—	—	—
Coastal Neutral—									
Charging Stock	125	250	—	0·941	7·7	0·895	—	—	—
Raffinate	—	—	91·3	0·930*	6·7*	0·883*	3	15	Trace
Extract	—	—	8·7	1·060	—	—	—	—	—
Californian Distillate—									
Charging Stock	800	300	—	0·957	19·8	0·897	—	—	—
Raffinate	—	—	25·4	0·872	8·5	0·799	1½	95	0·02
Extract	—	—	74·6	0·987	—	—	—	—	—
Mid-Continent Steam Refined Stock—									
Charging Stock	125	400	—	0·927	42·6	0·847	—	—	—
Raffinate	—	—	85·8	0·903	26·0	0·821	7½	78	1·0
Extract	—	—	14·2	1·08	—	—	—	—	—
Mid-Continent Neutral—									
Charging Stock	300	150	—	0·902	6·8	0·852	—	—	—
Raffinate	—	—	78·3	0·870*	20·0 (at 130° F.)*	0·815*	3¾	100	Trace
Extract	—	—	21·7	1·02	—	—	—	—	—

* Dewaxed raffinate.

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where 96 per cent. of the propane is removed overhead, cooled and condensed. The raffinate then passes through heat exchangers to a second propane evaporator working at 45 lb. per sq. in. The residual oil is then heated in a pipe still to 410° F., and by a combination of atmospheric and vacuum distillation towers cresylic acid and final traces of propane are removed. The extract phase proceeds through a secondary propane evaporator to a pipe still, then through atmospheric fractionation, steam stripping and vacuum towers.[25, 26, 27] The flexibility of this process is illustrated by the data for a wide range of distillate and residual oils given in Table XII.

TABLE XIII.

Process.	Company.	Refinery Location.	Date of Installation.	Estimated Capacity (Barrels Charge Daily).
Liquid SO_2	Associated Oil Co.	California	1924	1000
	Shell Oil Co.	,,	1929	3000
	Texas Co.	Texas	—	1000
	Tide Water Oil Co.	New Jersey	1931	2000
	Union Oil Co.	California	1934	1200–1500
	Argentine Government Oil Fields	Argentine	—	1050
	Burmah Oil Co.	Burmah	—	1750
	Min. Oelwerke Rhenania	Germany	—	42
	Rhenania Ossag A.G.	,,	—	1750
Phenol	Standard Oil Co.	California	1934	3580
	,, ,,	Louisiana	1934	5200
	,, ,,	New Jersey	1934	1000
	Imperial Oil, Ltd.	Canada	1930	2000
	Standard Franco-Americaine	France	1933	1500
Nitrobenzene	Atlantic Refining Co.	Pennsylvania	1934	2350
	Sinclair Refining Co.	New York	1934	1000
Chlorex	Bradford-Penn Refinery Co.	Pennsylvania	—	300–500
	Mid-Continent Petroleum Corp.	Oklahoma	1932	215
	Pennzoil Co.	Pennsylvania	1934	1000
	Socony-Vacuum Co.	New York	1934	1600
	Standard Oil Co.	Wyoming	1932	500
	,, ,,	Illinois	—	1000
Furfural*	Indian Refining Co.	Illinois	—	1500
Duo-Sol	Gulf Refining Co.	Pennsylvania	1934	1500
	Magnolia Petroleum Co.	Texas	1934	2030
	Socony-Vacuum Co.	New Jersey	1934	3000
	Herbert Green & Co., Ltd.	England	—	1000
	Shell Petroleum Corpn.	Illinois	—	2500

* Further plants since constructed.

A general survey of solvent extraction plants is given in Table XIII.[28] This list refers to plants in operation or under construction, but is not necessarily exhaustive.

Department of Oil Engineering and Refining,
University of Birmingham.

* Dewaxed raffinate.

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[28] Ziegenhain, *Oil & Gas J.*, 1935, **33** (45), 83.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Sixty-eighth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, London, on Tuesday, December 10th, 1935, the Chair being occupied by MR. J. MCCONNELL SANDERS, Vice-President.

AWARD OF STUDENTS' MEDALS AND PRIZE.

THE CHAIRMAN said it was his pleasant duty to present the students' medals and prize. The Council had awarded the students' medal and prize to Mr. H. T. Lorne, B.Sc., A.R.C.S., for his Paper on "The Adsorbent Action of Certain Natural and Treated Earths upon Bitumen and its Constituents."

Mr. Lorne was a former student of the Royal School of Mines, and had been elected a student of the Institution in January, 1935.

THE CHAIRMAN then presented to Mr. Lorne the medal and prize, amidst the applause of the members present.

He said that this year the Council were in the position of being able to present the prize which had been so kindly offered by Mr. T. C. J. Burgess. The first award had been made to Mr. B. O. Lisle, for his Paper on "The History and Development of the Tankship."

Mr. Lisle had been elected a student of the Institution in 1934, and thus, after one year, had succeeded in capturing one of its prizes.

THE CHAIRMAN handed Mr. Lisle the prize amidst the applause of the members.

ELECTION OF PRESIDENT.

THE CHAIRMAN remarked that the President of the Institution was elected by the members of the Council prior to each Annual General Meeting, and the office of the President commenced immediately after the close of the Annual General Meeting.

The Council of the Institution had that day elected Sir John Cadman as President of the Institution for the year 1936–1937, and he was pleased to be able to announce that Sir John had expressed his willingness to accept the office for a second term.

ELECTION OF VICE-PRESIDENTS.

THE CHAIRMAN said the Vice-Presidents of the Institution were elected from among and by the Council prior to each Annual General Meeting.

For many years it had been the custom for the Vice-Presidents to be elected at the December Council Meeting, to take office from the following April for the ensuing period of twelve months.

The Council had that day accordingly elected the following to be Vice-Presidents for the Session 1936–1937, to take office after the Annual General Meeting on 10th March, 1936: Lt.-Col. S. J. M. Auld, Ashley Carter, C. Dalley, Prof. A. W. Nash, J. McConnell Sanders, and Dr. F. B. Thole.

The following papers were then presented for discussion:

"Computations for Counter-Current Solvent Extraction Processes." By T. G. Hunter, B.Sc., A.R.T.C., A.I.C., and A. W. Nash, M.Sc., M.I.Mech.E., M.I.Chem.E., F.C.S.*

"Characteristics of Solvent-Refined Motor Oils." By Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.†

"Solvent Extraction Processes." By W. R. Wiggins, B.Sc., and F. C. Hall, M.Sc., A.I.C.‡

DISCUSSION.

Mr. F. E. A. Thompson said he would like to ask Mr. Hunter a question referring to the last table. In the calculation of the volume per cent. of solvent in the layer, the authors show that the amount of solvent in the raffinate layer increased as the amount of solvent treatment was increased, which meant that the solubility of the paraffinic material increased as its paraffinicity went up. It seemed extraordinary that this should be so, and he would like to know how, exactly, the authors had carried out the calculation.

Mr. T. G. Hunter said he was not sure of Mr. Thompson's point.

Mr. Thompson said that in column 7 of Table II, the "calculated volume per cent. of solvent in the layer" started off at 14·0, then decreased to 12·5, after which it increased to 14·5, whereas the "actual" figures for per cent. solvent in the raffinate layer fell to 9. If the calculated figures were correct, it meant to say that the raffinate of 0·799 V.G.C. was more soluble in the nitrobenzene than the raffinates of much higher V.G.C. In other words, as the raffinate became more purely paraffinic in type, so its solubility in the solvent increased, contrary to all previous findings in this respect.

Mr. T. G. Hunter replied that in this particular case the calculated figures were somewhat at fault, owing to experimental error in the determination of the equilibrium relationships used for plotting the binodial curve. In order to obtain equilibrium data for the portion of the binodial curve immediately adjacent to the base of the triangular diagram, batch extraction experiments under conditions resulting in rather small amounts of the raffinate phase have to be employed. In handling and analysing these small quantities of raffinate phase the percentage experimental error increases, and the lower left-hand section of the binodial curve close to the base of the triangular diagram may be, as in this particular case,

* See pp. 49–56. † See pp. 57–77. ‡ See pp. 78–98.

somewhat at fault. This error can be avoided by employing large amounts of oil and solvent in the initial extraction experiments. In this particular case accurate extraction data, obtained by the use of large amounts of oil and solvent, for the construction of the binodial curve were, unfortunately, not available, and hence the calculated percentage of solvent in the fourth and fifth lines of column 7, Table II, are too high.

Dr. R. Lessing said he felt very gratified by the fact that the whole subject of solvent extraction had been brought up and discussed in the three useful papers which had been submitted that evening, because it fulfilled an old dream of his which he had mentioned in a very hesitating manner some twenty-five years ago, when dealing with the analytical side of hydrocarbon examination in one of the standard text-books on commercial analysis. He had then realized that the ordinary methods of distilling hydrocarbons in order to find out something about them could not possibly lead to ultimate success, and that methods not based on thermal processes were necessary to investigate that very peculiar mixture, raw oil. To-day solvent extraction was a process confined to lubricating-oil treatment. Personally, he believed that in time to come it would go very much further. In oil, as in coal, there were mixtures of a very complex kind. As in some of the work he had done on coal, so he found that whenever he handled petroleum, exactly the same problems faced him—namely, that the ordinary methods of treatment were applied to mixtures which ought to be separated before any particular separation according to temperature began. He foresaw that it would be possible, if not with raw oil, at any rate with oil which had been freed of its lighter fractions, to arrive at processes which separated types of hydrocarbons from each other and from other chemical compounds present, prior to refining. It was quite possible that commercial means might be found for treating separated portions to greater advantage, even if, in order to comply with commercial exigencies, the products might have to be re-mixed afterwards.

Personally, he had had experience of solvent extraction in quite a different field, because during the War, when the question of oil supply had become rather an urgent one, and when it had been necessary to make better use of the then available home resources, which was ordinary coal tar, he had worked out a process (unfortunately not too efficiently) of separating the oil from the pitch in the tar by what was practically the old analytical method of asphalt and asphaltene precipitation. The very conditions shown in Mr. Hunter's Paper also applied, except, owing to the ignorance which then existed, it had not been possible to bring the work to fruition as had been done since by the application of a great many brains.

However, it had led to some result in the work done at the Chemical Research Laboratory at Teddington under the brilliant leadership of Professor Morgan, who had started actually on that particular reaction in elucidating the compounds present both in high, and particularly in low, temperature tars. What had been possible with a mixture complicated by the presence of oxygenated and nitrogenous compounds, should be possible with petroleum oils of various origins.

That work, although it had not been taken up by the tar industry in a practical way—that industry being very much slower to move than the oil

industries which had produced results like those reported that day in the space of about six years—had led certainly to the establishment of one chemical process—namely, the production of Resorcinol, which was to-day obtained almost exclusively in this way.

Mr. W. E. Gooday said that the account given of solvent-refined motor oils by Colonel Auld raised one or two questions and stimulated a few comments.

Perhaps the most interesting statement in the paper was in relation to a result that was scarcely to be anticipated—namely, that the solvent-refined lubricants compared favourably with their predecessors as regarded coefficient of fluid friction.

There were certain parts of the paper that, in his own opinion, called for qualification, and where the author's views were at variance with experience and current practice.

It was stated that the paper had been written "to see how the products behave under present methods of laboratory inspection." These "evaluating methods at present in use" were subjected on the whole to an unfavourable criticism as being insufficiently informative, and then conclusions were reached that extended well beyond the laboratory, be it physical, chemical or mechanical.

He thought Colonel Auld must admit one of two propositions, either: (1) the test results could not be translated into reliable terms of prospective performance because the methods of test were imperfect: from which it followed that no reasonable conclusions could be reached from the work he reported; or (2) the characteristics, so far as they went, were reliable, and the conclusions reached from them uninfluenced, "no doubt, by the particular interests of source of production involved," were true: in which case, his argument against intelligent specifications displayed excessive "volatility."

Later, the author threw away half the laboratory with a gesture that might lead to unfortunate misrepresentation outside the circle of our own profession. With some reason, the author rejected colour, but with more reason, inserted it before the massacre of tests on p. 60. Personally he thought it would be fairer were the author to say that of all the characteristica for which tests were usually applied, there was not one alone or two together that would disclose all one wanted to know, but that by taking a number of different tests—varied according to the service for which the oil was selected, *and in conjunction with practical experience*—one could approximate so closely to a reliable specification that one was entitled to describe it as "selective."

Wilson and Keith's classification existed not merely as a list of important properties, for when those properties had been measured by the best means available, figures were obtained, and those, with other numbers fittingly balanced, possessed a recognizable significance in evaluating the product to which they referred.

Colonel Auld was much too genial with Pour Point in saying that it "represents the behaviour of the oil under conditions of cold," but not generous enough when he said that it had "little significance in the present discussion." If they were discussing solvent-refined motor oils, it was assumed they meant finished products, in which case Pour Point—one of

the accepted criteria—should be included in the comparisons. If they were concerned with process only, then the effect of solvent-refining and subsequent dewaxing on the Pour Point was particularly interesting.

Under Viscosity Index the phrase " high enough viscosity to give good lubrication " took him (Mr. Gooday) back to some very early specifications, savouring of obsolete text-books, and he questioned whether in the following paragraph it was fair to those who would read the paper to describe paraffin wax as one of the viscous hydrocarbons under discussion.

Under Carbon Formation, as the reference might be read to include internal-combustion engines generally, a word should be added concerning fuel as a contributory factor in deposit formation, be it carbon or gum.

References to the Air Ministry Test would give no offence.

In dealing, under Results, with Viscosity Index, a caution appeared : " to hold a careful balance between all the properties desired in an oil and to see that their attainment is kept in perspective with practical value and ultimate cost." This balance was secured by the intelligent use of test results, and was reflected in carefully prepared technical specifications.

Tables I and II—for the sake of uniformity he suggested that " Saybolt " should be translated into " Redwood."

The two lines of text below Table V should not be necessary as they stood in a technical paper.

It was stated that mechanical tests were not yet recognized in determining lubricating value, but the author quoted such tests as showing whether solvent-refined lubricating oils had lost film-strength and *Lubricity*. This surely meant Lubricating Value, Oiliness or Slipperiness, although the *Oxford Dictionary* gave as alternative renderings : " Wantonness and lewdness ! "

The use of the word " repeatability " a few lines down called to mind the critic of Latinized English, who, complaining of the " penetrability of matter," translated it as " thoroughfaresomeness of stuff."

In reference to " what the oil does to the engine," Colonel Auld said : " whilst it may be possible to deduce this with some accuracy from the laboratory tests, none has yet been devised which can take the place of a test in an engine." Here they reached *rapprochement*, but while something had been heard about an oil with a name like " three-in-one," he did not think that even the engine test provided the ideal criterion of " all-in-one."

It was satisfactory to observe from the author's last line that engine tests " accord with the results obtained by chemical and mechanical tests." Colonel Auld arrived at where he wanted to get by means of tests that were no good, but they were useful.

He desired to add one word lest it be concluded that he was an advocate of rigid specifications : those works of art—gradually being metamorphosed into technical products—must be subjected to periodic review in order to keep pace with manufacturing developments. That they were not quite as ineffectual as Colonel Auld would have one believe was evident from their adoption by Admiralty, Air Ministry, U.S. Government Departments and many technically informed industrial concerns.

Colonel Auld's subject was an extremely interesting one, and he offered him his personal thanks and appreciation.

In conclusion, he would add the thought that despite the introduction of this new method of refining, their products would still be controlled by: (1) the type of crude employed, however wide the range might become; (2) the accuracy of application of the process, particularly in view of its flexibility; and (3) the economic exigencies, whatever they might be.

Mr. J. A. Oriel, referring to the paper by Messrs. Wiggins and Hall, said there were one or two points he would like to mention. The first point was where the authors spoke of the solvent power being increased by raising the extraction temperature, this only being effected at the expense of selectivity. Where they referred to the furfural process, the authors showed there that external cooling of the extract phase and re-cycling of the separated oil improved fractionization and yields. He thought it was quite well known in the literature that there were certain of the lubricating-oil firms which were using extraction processes—essentially the single-solvent process—who were finding that by the use of some sort of temperature drop, as indicated, they were enabled to get a better yield without losing the selectivity, as suggested in item 3.

The next page worried him as an operator of such processes. The authors indicated the toxicity of these various processes, and mentioned Chlorex as being of low toxicity. Personally, he happened to have noticed recently in the *National Petroleum News* that "Chlorinated hydrocarbons used in selective solvents produced headaches, nausea, nervousness, mental confusion, fatty degeneration of the liver and kidneys, loss of consciousness, coma, and finally death." As an operator, he felt that if that was the description of low toxicity, what about phenol and the other compounds which were marked down as toxic!

He felt that perhaps the paper might have been used to give the refiner some idea of the comparative value of the single-solvent process and the double-solvent process, because the petroleum literature was very voluminous nowadays in the comparison of the two processes, and each process was claiming something for itself. He thought it might be assumed that the single-solvent processes could be lumped together, as although some of them might give better results with particular crudes, in the main the processes were the same; and, for a given efficiency measured by something like the V.G.C. as against the yield, they probably all yielded just about the same; whereas the double-solvent process was something which was quite different. It was claimed that the double-solvent process has a greater flexibility, in that it could extract reduced crudes as well as distillates; but that claim, he felt, was perhaps a little over-done, because, after all, the cheapest method of removing undesirable constituents in an oil was distillation, and if by distillation one could avoid part of the expensive de-asphaltizing and other work which was done in the double-solvent process, it was probably an advantage.

Another claim was that, unlike the solvents in the single-solvent process, the solvents were not expensive.

The great point which he saw against the double-solvent process was that it was very expensive to install and expensive to run. There were two solvents, and, as a result, all the work was duplicated, in that one had to distil off both solvents (one a particularly difficult solvent) from the raffinate

and from the extract, whereas in the single-solvent one had merely the two distillations—the removal of the solvent from the raffinate and extract.

The authors did give some idea of costs in certain cases, and it would have been interesting, from the refiners' point of view, to have had that point extended a little. The costs for operating the single-solvent process varied from about 8 cents a barrel up to 20 cents, as given in the paper, and the best he could find in the literature for the cost of the double-solvent process was that it varied from about 45 cents to 80 cents a barrel.

It appeared to him, comparing the list of plants which were in existence at present and given in the paper with the latest list he himself had seen, that obviously the single-solvent seemed to be gaining a great deal of ground. Actually, the latest list given in *The Oil and Gas Journal* showed, excluding SO_2 plants, eighteen single-solvent plants, as against only five double-solvent plants. In that connection he might mention that the furfural plants now numbered five, one very large one having been built for the Gulf Refineries and one being built for the Shell Company in this country.

He would like to ask Colonel Auld one question, quite unconnected with these questions of extraction—namely, whether his remark concerning vacuum distillation, that the oils produced by vacuum distillation still contained unstable elements to a greater extent than in fact they would have done if produced by a harsher form of distillation—was based on experience and figures which Colonel Auld could quote, or whether it was merely an opinion based on the intuition of the petroleum technologist.

Mr. C. I. Kelly remarked that the advent of several new solvent processes for the manufacture of lubricating oils had created some confusion because of the mass of details for each specific process. Comparison of them with others employed for the preparation of lubricating oils for the world markets had added to the confusion; this could be avoided largely if they were collectively regarded as "arithmetical" methods, falling under the headings "addition" and "subtraction."

In conventional refining, the asphaltic compounds are "subtracted" by distillation from the lubricant fractions (at the same time, the residual asphaltic fraction retains valuable amounts of the high molecular weight, high viscosity lubricant hydrocarbons naturally occurring in the parent crude). The lighter coloured distillates are then treated with sulphuric acid, which is seldom, if ever, completely "subtracted" from the oil—to the detriment of the stability of the finished oils.

These products are supplied to the trade in various forms. Some are treated with addition compounds, each of which is intended to exaggerate some specific property; a few are intended to counteract the harmful effects of the unstable hydrocarbons, or of the small amounts of acid soaps not removed during refining. Others are added to low-viscosity oils artificially to enhance the viscosity index.

The former can be dispensed with in the majority of the applications of mineral lubricants, by refining the crude lubricants by solvent methods; the same argument can be applied to the latter addition agents also, because by making the necessary adjustments, the solvent processes can produce high viscosity index products from low V.I. charging stocks.

On the other hand, there are lubricants made by methods of subtraction; all the solvent-refining processes can be listed in this category of "subtraction" because they all aim at subtracting from the unrefined oil, the asphaltic compounds, the unstable hydrocarbons so detrimental in most instances to efficient lubrication, and the low viscosity index fractions. The removal of these unwanted constituents is performed in these processes at substantially low temperatures, which is reflected in the chemical stability of the finished products.

Solvent processes, however, differed among themselves, so that it would be too presumptuous to say that the products from each were alike.

These processes can be separated into two classes—namely, those which treated the lighter-coloured distillates, and those which were capable of handling dark residual oils. They can also be classified as "single" and "multiple" solvent processes—those which used one or two solvents respectively. The adoption of either classification does not alter the issue, because "single-solvent" processes were applied solely to "distillates," and the "two-solvent" process to dark residual charging stocks. It is important to note that the converse of this statement was only partly correct, because, whilst single-solvent processes cannot be applied to residual charging stocks, the two solvent, or Duo-Sol process, can refine distillate oils.

Consequently, inasmuch as it is very flexible, and that it is able to handle any type of charging stock—distillate or residuum—the Duo-Sol Process stood in a class of its own.

There is another advantage to be gained by the use of the "two-solvent" process as compared with the single-solvent methods. The latter require "distillate" material, in the preparation of which a considerable percentage of the lubricant hydrocarbons naturally occurring in a crude oil is rejected in the residual asphaltic fraction.

By treating the whole lubricating oil content of a crude oil in the "Duo-Sol" Solvent process, the refiner can include in his finished product the high-molecular weight hydrocarbons which have been proved extremely valuable lubricants.

The "quality" of these oils has been discussed, and he desired to thank Colonel Auld for expressing the subject very fully in his paper. Colonel Auld had referred in detail to the several features and properties to be looked for in a good lubricating oil. He did not intend, however, to enter into the discussion whether the results of laboratory tests could be applied, by inference, to the judgment of the oil's quality in conditions of service.

He had reached a conclusion on the service quality of these oils during a recent visit to the U.S.A. He had had the opportunity of meeting refiners operating solvent processes, who had expressed their views as to what the oils were good for; on the other hand, he had also had the opportunity of visiting *several users* from whom he had been able to learn that most of the claims made for solvent-treated oils were substantiated in practice.

In one particular instance, he had visited an airway company which experienced serious competition from another air line. Their difficulty was that their older engines were not capable of providing safely the extra power to give the higher speeds of the newer aircraft used by the other

aviation company. He had been gratified to find that by the use of the high viscosity-index, chemically stable solvent-refined oils, this aviation company had not only met the severe competition satisfactorily, but had also experienced savings in maintenance and repair charges.

It would also interest those present to know that the air-arm of the U.S. Navy Department had been using solvent-treated oils in their craft for the last three years.

Further, it should be noted that the uses of solvent-refined oils were not necessarily limited to the automobile and aircraft industry. (At present, the major portion of solvent oils was used by these industries because the supply of them was extremely limited.) He had obtained definite proof, in the case of one type of solvent oil at least, that they had been applied with every success to industrial lubrication uses.

Colonel S. J. M. Auld, in reply, said he expressed his appreciation of Dr. Lessing's remarks and Mr. Kelly's. He had found some difficulty in following Mr. Gooday's witty but encyclopædic manner of discussing the particular aspect of "specifications," but did not take it entirely seriously. He thought it would be generally agreed that he (Colonel Auld) had gone out of his way to point out, regarding the tests and trials mentioned in his paper, that the results were left for one to reach one's own conclusions. There was no question of putting up new standards, unless those standards were found actually to represent things in practice; and that, again, was largely outside the sphere of the present paper.

As regards the use of Saybolt viscosities, that was a thing which he personally disliked in this country, but in the present case it was done deliberately, because they were the figures employed in the calculations of Viscosity Index and indicative of the characteristics of oils from the same American sources refined by different methods.

In reply to Mr. Oriel with regard to vacuum distillation, he admitted this was largely a matter of opinion and general experience. But it was an opinion largely shared on both sides of the Atlantic, not merely by producers, but by users, with regard to the possibility of producing by vacuum distillation materials which were not quite as stable as one would like them to be.

The meeting then terminated.

Messrs. W. R. Wiggins and F. C. Hall, in reply to Mr. Oriel, wrote:

There appears to be an optimum temperature for the extraction of any particular type of lubricating oil stock by a given solvent. It is therefore preferable, in a continuous or multi-stage extraction process, to adjust the temperature of extraction through the system so that at any stage the optimum conditions are obtained corresponding to the composition of the oil at that point. This represents, in effect, the use of a temperature gradient, as in the furfural and other processes, whereby the ingoing stock is extracted at a lower temperature than the outgoing, more paraffinic, raffinate.

With regard to the toxicity of these selective solvents, it is difficult to fix any satisfactory scale by which the toxicity hazards involved in handling such solvents may be represented. Reasonable care is essential, even with

relatively non-toxic materials, since prolonged exposure to the majority of solvent liquids is undesirable. So far as chlorex itself is concerned, this is stated to be somewhat more toxic than carbon tetrachloride for equivalent vapour concentration, but the lower vapour pressure of chlorex reduces the hazard.

At this early stage of development it is difficult to give adequate comparisons of the single- and double-solvent processes. In general, the single solvents are better adapted to distillate oils; but propane de-asphaltizing followed by single-solvent treatment appears to yield results with residual stocks in many cases comparable with those obtained with the double-solvent process.

Dr. W. E. J. Broom, in a written contribution, said:

During the discussion of Colonel Auld's paper regarding the "Characteristics of Solvent-Refined Motor Oils" exception was taken by one speaker to the use of Saybolt Universal viscosities for the presentation of data. Colonel Auld, in reply, referred to the fact that this system is used in calculating viscosity indices. Reference to Table III in the paper shows that results are quoted in Redwood seconds for various oils of which the viscosity indices are also given. It would appear more desirable to give Saybolt viscosities where V.I.'s are quoted, since the determination of V.I. from Redwood seconds involves a calculation which is subject to some degree of uncertainty. For example, the figures quoted in Table III by one method of conversion yield V.I.'s which in three instances are markedly different from those reported. The use of Saybolt seconds would obviate this uncertainty in conversion, and is therefore to be preferred.

Mr. O. T. Jones, in a written contribution, said:

Every good purpose will be served by the co-operation of oil technologists and mechanical engineers in regard to lubrication problems. The mechanical engineer sometimes feels that the oil technologist pays too much attention to laboratory characteristics of oils. Experiences met with in practical engineering do not in every case compare with laboratory results; consequently, there is every need for mutual understanding.

Some interesting information on the temperatures of pistons has recently been published. An air-cooled motor-cycle engine of $3\frac{3}{4}$-inch bore was shown to develop a temperature of 304° C. at the centre of the piston when running at 4000 r.p.m. with an air-cooling draught of 50 m.p.h. The same engine, running under the same conditions but with an air-cooling speed of 77 m.p.h., developed a temperature of 262° C. at the piston centre. It is understood that the engine was running under full throttle conditions on the test bench. The difference in temperature between the centre of the piston head and the outer edge of the piston crown was 44° C., and the difference in temperature between the edge of the piston crown and the cylinder barrel was 59° C. The estimate formed during these tests as regards the amount of heat removed from the piston by oil spray and air turbulence was in the region of 20 per cent. at 3000 r.p.m.

While these tests apply to an air-cooled engine of the high performance type, it is interesting to note that, as regards large air-cooled aircraft engines fitted with aluminium alloy cylinder heads, the cylinder tempera-

ture at the sparking plug boss, the thermo couple being fitted beneath the sparking plug, is between 200° and 220° C., whereas, with air-cooled aircraft engines having bronze cylinder heads, the temperatures at the same location may be between 250° and 300° C. It is apparent, therefore, that under these conditions piston temperatures would be very considerably higher than those shown by the tests on motor-cycle engines.

The author in his remarks has referred to the importance of lubricating oils which resist the effects of heat in automobile and aircraft engines, and in this respect Table VII in his paper is of particular interest, bearing in mind that the ingoing oil temperatures in modern aircraft engines, when tested under Air Ministry conditions, is 70° C., and the outgoing temperature may be from 110 to 120° C. It is well known that the temperature of the oil leaving the big-end bearing is considerably higher than that of the ingoing oil, whilst the temperature of the oil leaving the pistons is still higher; therefore, the figures shown in Table VII have a distinct value in regard to some of the problems met with in the lubrication of high-speed internal-combustion engines, whether of aircraft or other types.

Referring to Table VII, the oil mentioned as Solvent-refined Aviation Oil (H) is known in practice to give particularly clean results under heavy duty conditions, and it is interesting to note that where this oil is subjected to oxidation tests higher than those at present established, its performance is superior to any of the other oils referred to, even where the temperature is as high as 250° C.

In the section referring to "Viscosity Index," the author refers to the importance of this being greater in regard to motor oils than aero oils. Aeronautical engineers will express some doubt about this point, because it is well known that oil distribution in aircraft engines, particularly in cold weather, is of major importance, and unless special care is taken in regard to the details of engine design, piston dryness is experienced due to inadequate quantities of oil reaching cylinder walls. Consequently, free-flowing oils are of the greatest importance, provided that these properties are secured without penalty in regard to the lubricating properties of the oils themselves.

It is well known that there is a time lag before adequate oil circulation to the pistons is obtained when starting up from cold in winter weather, both in aircraft and motor-car engines, excepting where special designs are incorporated. With a normal grade oil in use the delay in regard to oil reaching the pistons in adequate quantities may amount to several minutes, so that the oil distribution feature in certain circumstances may be of much greater importance than that of easy starting. In regard to motor-car engines, the question of difficult starting is one that is obvious to the motorist, whereas insufficient oil circulation will result in increased rate of wear, which only makes itself apparent some time afterwards.

Following Table III is a reference to S.A.E.30 as a distinct summer grade. This only applies to engines fitted with cast-iron pistons; for those fitted with aluminium alloy pistons, S.A.E.40 and 50 are usually regarded as summer grades where the other details of the engine are normal, *i.e.* in connection with design of lubrication system, etc.

Following Table X, reference to mechanical tests is made. The writer arranged certain tests at the National Physical Laboratory in regard to certain types of double-solvent treated oils, and certain other oils of normal

manufacture, both compounded and mineral. In determining what tests should be made, it was decided to adopt the Jakeman test on the N.P.L. machine because this test is carried out over a period of fifty hours under high bearing temperature conditions. Moreover, during the test the oil is circulated and subjected to oxidizing conditions, and it was felt that such tests would be far more convincing to the mechanical engineer than certain others which are of comparatively short duration, and which have little reference to practical engineering experience. It was particularly interesting during these tests to observe that two oils which had reasonably similar laboratory tests showed a difference of nearly 100° C. as regards seizing temperatures.

In this connection he referred to Table XI of Colonel Auld's paper, particularly in connection with the first column under heading Solvent-refined, and the third column under No. 1, in regard to Conventionally-refined Oils. It will also be noted that under these conditions the minimum coefficient of friction was 0·00067, as against 0·00095. In some cases normally refined (compounded) oils have even higher coefficients of friction, thus showing that the right type of solvent-treated oil may have a co-efficient of friction approximately 30 per cent. lower than certain other motor oils. As it is common knowledge that the mechanical efficiency of the average internal-combustion engine of the motor-car type is in the region of 80 per cent., this is a very important matter.

In addition to the foregoing friction and seizing temperature tests, a 100-hours bench test in a standard motor-car engine was undertaken at the National Physical Laboratory. This engine was of the 12-h.p. type, and in order to put the lubricating oil under as severe running conditions as possible, the oil-sump temperature was maintained throughout the test at approximately 100° C. This test was run at an engine speed of 2500 r.p.m., the engine developing 12·5 b.h.p., which corresponded to a car speed of 42 m.p.h., the load being equivalent to that required to propel a saloon car at that speed. The oil consumption after 100 hours' running (equivalent to 4200 miles) was slightly less than half a gallon, whilst the wear measurements showed extremely small change before and after tests, averaging from one ten-thousandth to one and a half ten-thousandths of an inch at the top of the cylinder bore. The crankpins showed no measurable change during the test, while the big-end bearing wear was only one ten-thousandth of an inch under these conditions. The carbon deposits in the combustion chambers were extremely small, whilst the general cleanliness of the engine in regard to the crankcase and oil circulation system was extremely good, no sludge having formed on any of the parts. It is understood that the loss in weight of the piston rings during the test was almost negligible. Deposits on valve stems were extremely small. It is believed that this is the highest temperature at which a motor-car engine has been run under independently observed conditions, and the low rate of wear, carbon and sludge formation would definitely confirm that solvent-treated oils, in addition to giving good laboratory characteristics, also show extremely satisfactory results in internal-combustion engines.

Colonel S. J. M. Auld, in a written reply to Dr. Broom, said that the use of Redwood viscosities in Table III was because the tabulation was to show

the effect of solvent refining on a complete series of commercial lubricating oils in this country. It seemed desirable that readers should see the effect of solvent refining in terms of units to which they were accustomed. The inclusion of the V.I.'s was only incidental. In this connection he wished to thank Dr. Broom for directing his attention to the V.I.'s as given in the preprint. These had been taken by inadvertence directly from the Saybolt viscosities broadly descriptive of the grades of oils, whereas it had been intended to calculate them back from the actual Redwood figures. The real readings, now included in the text, showed in nearly all cases a still greater difference in V.I. between solvent-refined and conventionally-refined oils.

In reply to Mr. O. T. Jones, he wished especially to thank him for his illuminating communication. The figures given by Mr. Jones for piston temperatures were very significant, and supported more than ever the feeling that behaviour of the lubricating oils under cracking conditions was of the greatest importance in providing a clue to their probable behaviour in the engine. That being the case, the similarity between the course of heat disruption and heat/oxidation disruption seemed to call for more severe conditions of test for the evaluation of high-duty motor and aircraft oils. It was consequently a fact of some importance that the higher the temperature of the heat/oxidation test the more marked was the stability of the solvent-refined oils.

In directing attention to the coefficients of friction of the solvent-refined oils, Mr. Jones had touched upon an interesting and important aspect of the effects of the new refining. In his paper he (Colonel Auld) had been content to indicate that whatever the value of mechanical tests, the solvent-refined oils appeared at least none the worse in that respect. In point of fact, there was a good deal of information available which went to show they were better. The reason was not obvious, and did not seem to accord with the generally accepted theories of the value of unsaturated bodies, whether polar or non-polar in configuration, as the explanation of oiliness. Such bodies might be expected to be found, or at any rate to be concentrated, in the extract during solvent refining. That the solvent-refined oils from mixed base crudes behaved as they did would lead one to assume the existence of some super-oily constituents present in small quantities, and of such preponderatingly paraffinic structure as to remain in the raffinate.

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THE OIL INDUSTRY AND THE WORLD CRISIS.*

By J. B. Aug. Kessler.

The consumption of oil products has increased very considerably during the years following the War. In 1924 in the United States it was not the question of too much oil that was calling for a good deal of attention from the Government, but the fear that at some time the supplies would be exhausted. It was in that year, 1924, that, at the instigation of President Coolidge, the United States Government appointed the Federal Oil Conservation Board to discover in what way this waste could be restricted and what reserves were available.

A few years later, however, the whole position had changed, and over-supply was absorbing their attention. In 1928 the American oil companies formed the U.S. Petroleum Export Association in order to try to keep order in the export markets. In the United States, however, it is illegal to regulate the production by arrangement between the companies, and, therefore, the plan failed, nothing being done to keep production more or less in line with consumption. The American Petroleum Institute realized that without any regulation of production one could not expect that a balance between supply and demand would be secured. They therefore submitted to the Federation a plan for world-wide rationing of oil production. The United States laws prevented this being carried out, however. Later the Federal Oil Conservation Board called a meeting of the Governors of the principal States, such as Texas, Oklahoma, California, etc. Legal difficulties again made it impossible to go ahead with any plans.

From May 1929 production in the United States was increasing very rapidly, and by August it had reached the level of 3,000,000 barrels a day. This was, of course, far too big a production. The different States were working individually, without any real co-operation, to reduce this production to a certain extent, and by the end of 1929 they succeeded in reducing it to 2,640,000 barrels daily. They went even further in 1930, and reduced it by one-third, to about 2,000,000 barrels daily. The stocks had, however, increased, and by May 1930 the level of 700,000,000 barrels was reached. The price levels had been undermined considerably. The Petroleum Export Association could no longer be maintained, and came to an end at the close of 1930.

The Rumanians now realized that it was also their own over-production that was undermining the price levels, and therefore the Rumanian oil producers tried to do something constructive. In 1930 they succeeded in reducing production to the 1929 level. In the second half of 1930 the over-production in the United States had so weakened the markets and the stocks were so enormous that the result was a drastic price decline. The whole Rumanian plan then, of course, collapsed, and all restrictions were withdrawn.

* An address given to the Students' Section (London Branch) of the Institution of Petroleum Technologists on November 19th, 1935.

In my opinion, these different efforts failed through lack of synchronization. Experience has taught us that control of production is extremely difficult, and that it is an impossibility without synchronization.

The year 1931 was disappointing. Legal difficulties in the United States made any progress impossible.

In 1932, the Russians, who had been exporting increasing quantities, felt that they were in a strong enough position to take the initiative, and they suggested a conference to bring themselves into line with the world's efforts. We had a conference with them in New York and talked things over, but it was found quite impossible to do anything. This failure did not stop us, and that same year we continued negotiations with the Rumanians. In the meantime the production in the United States had been kept on a more stable level and prices went up a little. This encouraged the main oil companies to further efforts. We felt that we must try to see if we could not bring about a sort of international agreement to cut down over-production. Oil, after all, is an exhaustible quantity, and a reduction of production to the level of legitimate consumption is really a service rendered to the world. Over-production of oil simply means waste for the world, and that means that we consume unnecessarily the reserves of future generations. Therefore, some equilibrium between supply and demand must be maintained. We got together with the Rumanians once more, and we put into effect an arrangement by which their production was stabilized. This came into effect on January 1st, 1933. Just at that time American production, which had been under satisfactory control, again got out of hand. A new factor then came into being, that of hot oil production—which means that on such production no royalties are paid, as it is produced illegally. Supplies were therefore increased to large quantities at the beginning of 1933, just when Rumania started to apply their conservation. In consequence of this rapid increase in United States production, prices dropped. For the second time the Rumanians found that by producing under agreement no better prices could be obtained for a smaller quantity, and therefore that world-wide arrangements were very disappointing. By the middle of 1933 there was no longer any agreement.

In 1934 the production was better controlled, but the stocks had become so large throughout the world that prices did not recover as quickly as we had hoped. In 1934 a new oil producer was put on the world's markets—Iraq—and provided more supplies of which the world had no need. Another feature, which was really the result of the world crisis, had in the meantime come into effect. Governments tried to become self-sufficient. It was the result of the confusion created by the world crisis, about which I will say a little more later on. The Government tried to encourage home-production of motor spirit from coal and the use of alcohol as motor fuel by outrageous protection, but both proved much too costly. All this aiming at self-sufficiency was, of course, the result of confusion in currency.

The history of the past five years, as I have tried to explain, has shown that the oil industry as a whole must co-operate to stop wasteful production, and thus reserve valuable oil for future generations. The fact that nothing very satisfactory has been achieved during those years in the matter of balancing production and demand, is due to a very large extent to the laws in the United States, which make international arrangements

extremely difficult, and also because of lack of synchronization. Even if these laws had not existed, however, and even if synchronization had been more practical, I do not think that the depression in the oil industry would have been avoided. It was the world crisis that was really the main trouble.

To return to the oil industry for a moment, however, as I said before, the consumption of oil increased after the War, but then demand fell again, with the result that we were over-producing. The decline in consumption was due to the world crisis. There the oil industry's crisis and the world crisis became connected.

Now for the cause of the world crisis. There are very many opinions, and I do not claim that mine is right—but in my opinion the world crisis is really due to the mismanagement of the monetary and credit system. That is rather vague, and I feel that here I must try to explain it a little. It is somewhat controversial. The right to consume is not just because you wish to do so. The economic right to consume must be derived from economically useful production. It was always like that. From the beginning of time it was quite clear that if you wanted to buy a loaf of bread, you could not get it without some return, and that something in return had to be something useful, and therefore desirable, that had been produced. Now everything is more complicated and far more scientific, but that principle still prevails. When society became a little more refined, it was no use changing a loaf of bread for a pair of shoes—if shoes were worn then. Money was used, and that money was gold or silver, and it was gold or silver because you could not get it unless you had produced something—and there you have the right to consume. Later on we got our banking system and we started to issue paper money. Then, later again, we found that paper money was really becoming old-fashioned, and we used cheques. The underlying principle, however, is still the same. There is no change at all, and the principle that honest money and credit must result from production, and economic production, is still true.

Now, how did we find the world after the War? If you only think of the tremendous War Loans—all those War credits and War indemnities—you will realize the state the world was in at that time. After the War we based the right to consume on all the money and credit which had been created for War production, and it took many years for the world to discover that these credits and this money were not honest money and credits—that, in fact, they might be called forged money and forged credits. Gradually, however, the world found it out, and the result was the same as if here in London a good many of the bank-notes were forged. Suppose that to-morrow we were to find that forgers had brought them into circulation and we had some of them in our pockets. We should try to pass them on and to get in exchange something which we knew could not be forged, preferably gold. That is what happened in the world when it was found that money and credits in circulation were not based on sound economic production. It was, from the point of view of those who had the money or who were creditors, perfectly natural to change that money for gold. They started to hoard it, and if gold is hoarded it gets dear, and if it gets dear, prices of commodities, expressed in gold, drop. That is why in my opinion everything fell in value, and therefore wages and taxes, and, in

fact, everything, got out of proportion to the price at which products could be sold. When that happened, of course, contractors and producers got into financial difficulties. Then we got unemployment, and governments started to protect the domestic market to prevent further unemployment, and no imports were allowed, and you got the trade obstacles that we all know so well. I do not think it was the trade obstacles which caused the crisis. The crisis was caused, I think, by this inevitable result of unsound world finance, caused by the War. If not, why were these trade obstacles not started in 1905, why not in 1890? It is my opinion that trade barriers are the logical consequence of the mishandling of the monetary and credit systems ever since the War.

This is the natural result of any war, and if we are unfortunate enough to see another war, we should again see the same results.

Now, that is my opinion as to what has caused the crisis. I must say that if we are to get out of the crisis, we must reverse what caused the crisis, and cure the monetary and credit systems so that there can no longer be any question of forged money or forged credits. In other words, I come very near the orthodox conservative finance, but that must not be applied too dogmatically. We must remember every moment that the unemployed and those who have very little to consume cannot understand the monetary system. Some, perhaps, have not enough wherewith to buy sufficient food, and therefore the sound economic demand for food has decreased. We cannot stop making food for them, however. Therefore, as long as things are difficult and as long as the world crisis continues, a certain amount of consumption will have to be allowed, although it is not economic in the right sense of the word. This consumption is not based on production, but will have to continue as long as the crisis lasts. Although in this country conditions are gradually improving, in other countries they are not. In the latter it will be necessary to make even more concessions in that respect than here. It is done, of course, everywhere; it is done in the United States on a large scale. In other countries, still on the pre-crisis Gold Standard, they try to go to the other extreme—wholesale deflation. The United States thought only of employment and consumption, and forgot about sound money. The countries on the pre-crisis Gold Standard did just the opposite—or at least said that they believed in the opposite, but did not do it. We know now, for instance, that even in France public works were started to create work in order to increase consumption. These public works, however, were not supported by sound money—that is, money which is the fruit of economic production. They are supported by money and credit created for that purpose out of nothing. The United States, on the other hand, are becoming (I think I may say) more constructive in money and credit matters. In other words, the two extreme conceptions are nearing each other.

That is what I think, and therefore, in my opinion, the cure of the crisis is to cure the monetary system, but that cure must be applied with sufficient common sense—we must deviate a little, or even much, from time to time from our sound basis of money and credit. During the first years of the crisis, I do not know how many revolutionary proposals have been made for its cure. The revolutionary proposals are now gradually disappearing again. Some of the best London newspapers opened their columns for the

most fantastic proposals about money and credit; but, fortunately, the same newspapers no longer print such unbaked stuff.

I think that the world has got to a point of very considerable prosperity under economic rules which we must not throw overboard too lightly. The crisis is gradually disappearing. Things are improving, and in the years to come we shall recover completely. If the world crisis is disappearing, the oil industry can expect to share in the growing prosperity.

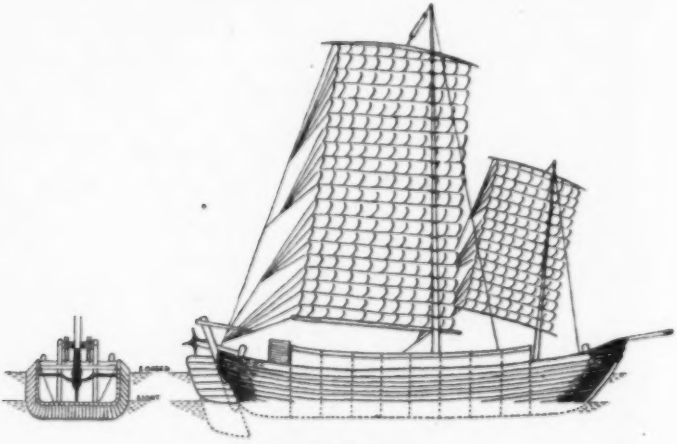
The oil industry is changing all the time. A good many years ago it was mainly dealing with kerosine. Now there are more and more products included, and consumers are still asking for more highly specialized products, and are, I think I may say, receiving them. The difference in the oil industry as it was, say, fifteen years ago, and as it is now, is amazing. We are in a revolutionary period in the development of the oil industry, and that is due to the marvellous achievements of the technical people and those who manufacture the products. There is, too, still a large amount of work to be done in that way by geologists, chemists, etc., who have a tremendous task ahead of them. Possibilities are almost unlimited. Those who have chosen the technologist's side of the oil industry as a career have, I am sure, chosen very wisely and well. It is one of the jobs of the future to work towards the further development of oil.

DEVELOPMENT AND HISTORY OF THE TANKSHIP,*

By B. Orchard Lisle (Student Member).

The tanker is the most efficient and economical means of moving both crude and refined products. The comparative cost per net ton mile in the United States—with its vast network of pipe-lines—is: by rail car, 8·3 mills †; by pipe-line, 3·2 mills; and by tank vessel, 1·25 mills.

Although the oil companies are the owners of vast tonnage, about £173,690,000 being invested in the 14,474,000 ‡ tons d.w. of ocean-going tankers—apart from smaller vessels—in service at the present time,



NEWCHWANG JUNK.

surprisingly few of the papers read and discussed where oil men gather deal with this important phase of the industry.

The *Newchwang Junk* was probably the first example of the bulk oil-carrying vessel. Originally built for the transportation of water in the beginning of the eighteenth century, the Junks were later used for petroleum—capacity being about 50 tons. The cross-section of this type of junk bears a marked resemblance to the present-day tank vessel. It was provided with a trunk for expansion and contraction of the liquid cargo, and to keep the main hold always full. While the *Newchwang Junk* did not have a centre-line division, her main hold was divided by transverse bulkheads.

Regulations for the carriage of oil in bulk, up the Volga, were issued by Peter the Great in 1725.

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* Paper awarded Burgess Prize, 1935.

† One penny (British) equals twenty mills. ‡ Approximate.

Jonas Hanway mentioned in 1753 that the Iranians loaded oil, collected near Baku, into their boats in bulk, which craft he described as being very leaky. How long this trade had been going on is not known, but it would appear that it was very old.

Petroleum had also been carried down the Irrawady (from the hand-dug wells of Burma) in the holds of the native sailing-boats to Rangoon for refining. They appear to have been used for that purpose until after the advent of the Burmah Oil Company. An account published by Col. Symes, in 1795, mentioned that "The celebrated wells of Yenangyaung supplied the whole Empire and many parts of India with that useful product—earth oil. The mouth of the creek was crowded with large boats waiting to receive a lading of oil."

Tate mentions in his book that "oil had also been brought from Burma to this country in vessels of about 1000 tons burthen, fitted with iron tanks."

Wooden tank barges were then being used on the Allegheny River, U.S.A. Because of the shallows, they were floated downstream in large fleets on artificially created freshets. They were divided into compartments, and were filled at the wells by means of leather hose. There were about a thousand such craft, resulting in a great number of accidents and preventing the proper development of these vessels.

Early that same year a Mr. Gibson of the Isle of Man had the *Ramsey*, an iron sailing tank-vessel, built to carry oil. The cargo space was divided into compartments by a centre-line and several thwartship bulkheads. Since they were completely filled, and were air-tight, there was no wash. She was fitted with a patent expansion device.

Rogerson & Sons, Newcastle, in conjunction with the Atlantic & Great Western Railway, formed the Petroleum Trading Company for the express purpose of importing oil into Europe, *by means of iron tank-vessels specially built for the purpose.* No particulars are available of their *first* vessel—but a few months after the construction of the *Ramsey* they built the *Atlantic*, followed by the *Great Western*, both holding about 700 tons of oil in eight tanks.

They were provided with transverse and central longitudinal bulkheads; expansion was controlled by the fore and main masts, which were of hollow-iron construction. They were evidently the first to carry their own pumps. The *Atlantic* was wrecked about six years after, but the *Great Western* operated until 1896, when she was abandoned at sea.

The *Charles* was a later ship fitted with iron tanks for oil carriage. The tanks were constructed to fit the interior moulding of the ship, and were either twelve or thirty tons in capacity, being worked on the separate tank system without pipe connections. Her total capacity was 794 tons. She operated from 1869 to 1872 carrying crude from the U.S.A. to European ports, being destroyed in the latter year by fire.

The first *tank-steamer* to be built was the *Vaderland* in 1872. She and her two sister-ships were built primarily as passenger vessels, and certain restrictions prevented them from ever carrying oil. While a definite step forward, no comparative experience was gained from them.

A 375-ton sailing tanker named the *Lindesnoes* was built that year. The hold itself formed the tanks, being lined with felt and having a central

bulkhead, as well as a number of thwartship divisions. Some iron tanks were installed in the tween-decks, but were later removed for barrel transport. Two other similarly designed Norwegian vessels were built at the same time.

When there was a great fall in prices seventy years ago Ludwig Nobel conceived the plan of transporting bulk-residuum to Astrakhan in a wooden barge, at the risk of loss by leakage. The leakage did not turn out to be as great as expected, and since the oil could be easily pumped in and out, the system was taken up by others. Refined products could not be carried thus, so the holds of some barges were lined with cement—in others were placed large iron cisterns.

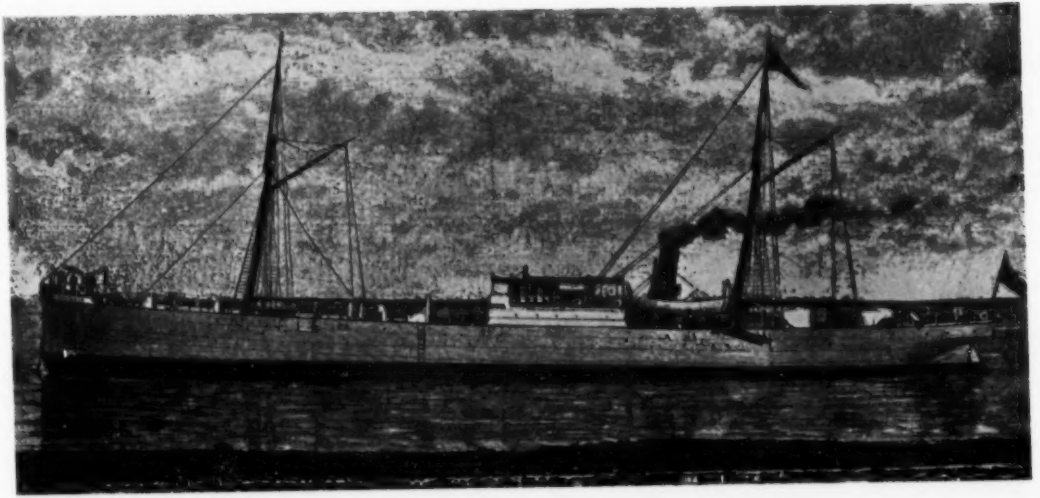
At first the barges and schooners so fitted were used for the Caspian only; but it was not long before the method spread outside the boundaries of Russia, furthering previous developments.

In addition, the credit for the first tank-steamer *to see actual service* must go to Nobel. She was the *Zoroaster*, built in 1878, with a capacity of 250 tons in twenty-one separate vertical cylindrical tanks for transportation of kerosine, and was built at the yards of Lindholmen-Motala, in Sweden. The tanks were later removed and the oil carried to the skin. Her engines were amidships and steam was raised by burning *oil-fuel*. No arrangements appear to have been made for expansion of the oil cargo.

Nobel's were making progress—for the next year they built the *Buddah* and the *Nordenskiold*. These two vessels had their engines slightly further aft, the tanks had expansion trunks, and were equipped with four longitudinal bulkheads and a number of transverse bulkheads. While they retained the double-bottom of former vessels, the oil was carried to the skin at the sides. Towards the end of the year Nobel's built the *Moses*, which had no double-bottom, and in addition to the other features had two cylindrical tanks over the propeller shafting.

Somewhat similar was the *Merkurii*, belonging to Rashmag of Olja, and, like the *Moses*, she was built by Lindholmen's. She had a large dry cargo space forward (which could also carry oil), aft of which were four kerosine tanks to hold 4920 poods and divided by two longitudinals and a number of transverse bulkheads. Each of the twelve compartments formed had a cylindrical feeder trunk which cared for expansion. Additional dry cargo was carried between the trunks. She had two similar tanks to those of the *Moses* abaft her engine-room, and 900 poods of astatki were carried in a double-bottom below the engine-room, probably for bunkers.

A ship not mentioned in previously published records, but which deserves notice, is the *Spasatel*, built for the Caspian Sea Oil Company in 1882 by Crichton-Vulcan of Abo, Finland, having a centre-longitudinal and three thwartship bulkheads. She was the first steam tanker to have engines in the *stern*, and one of the first to have a cofferdam separating the oil tanks from the engine-room, but this could be, and was, used for oil cargo. She had two main tanks holding 27,800 poods and a dry cargo hold forward, which was piped and held 14,000 poods of oil. An additional cylindrical oil tank was constructed on the deck amidships, with a small trunk for expansion. The deep hatches cared for expansion in the main tanks. She had no double-bottom under the oil tanks, but there was a



EARLY RUSSIAN TANKER OF THE MOSES TYPE, 1882.

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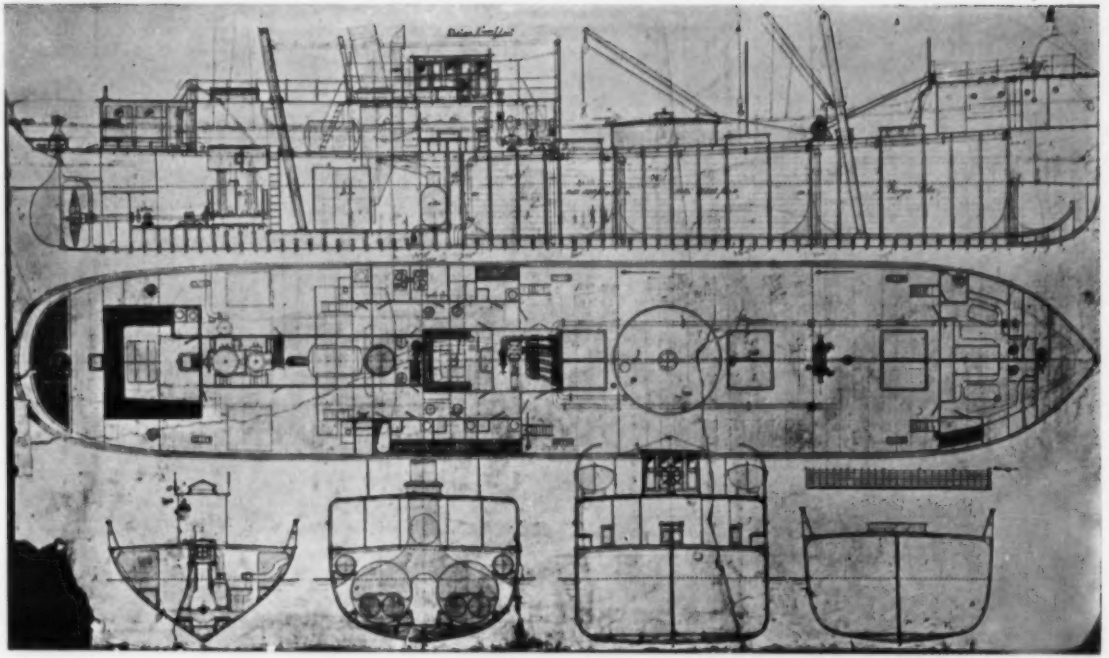
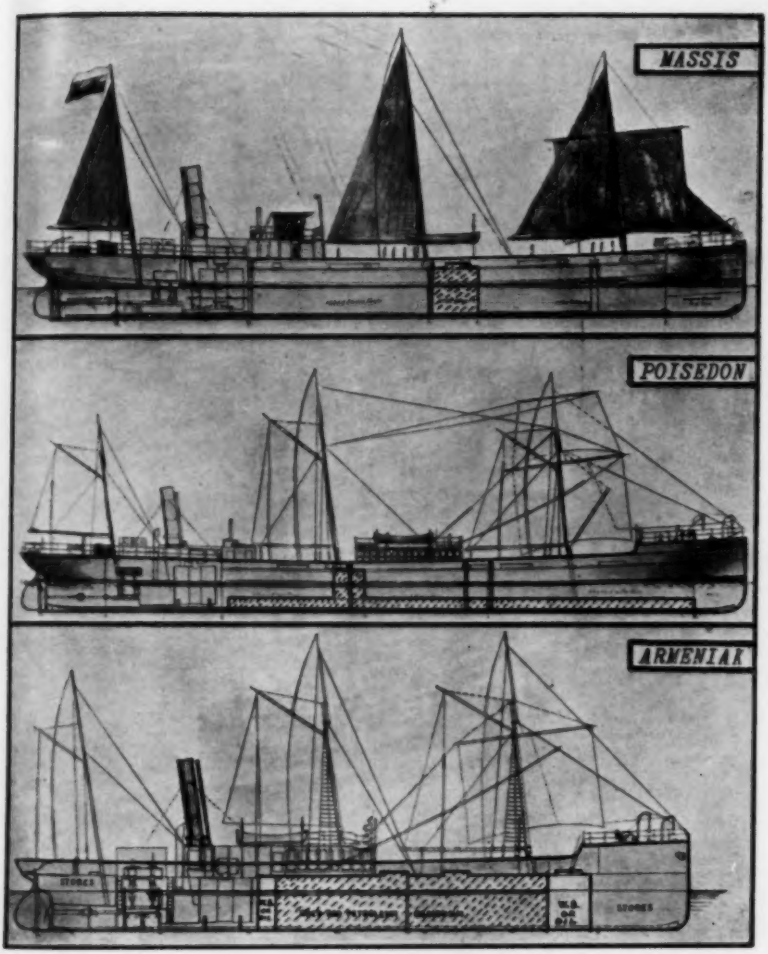
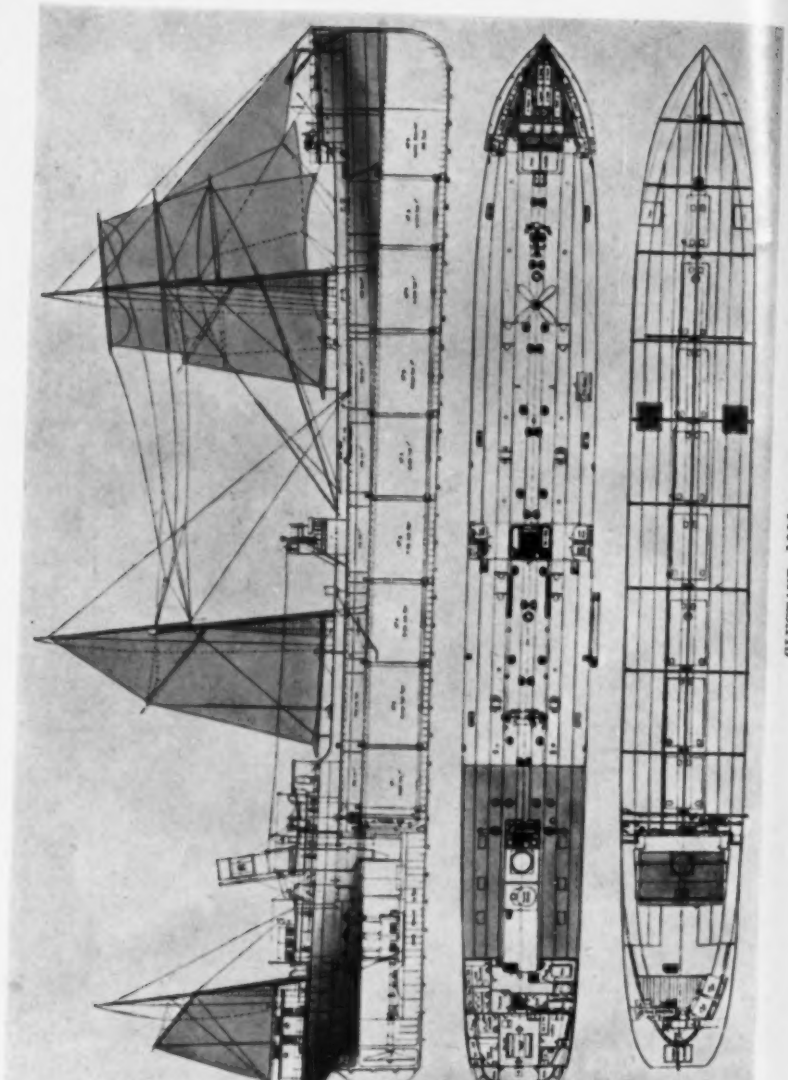


SPASATEL, 1882.



THREE VESSELS BUILT IN 1883 FOR CASPIAN SERVICE.



GLUCKAUF, 1886.

double-bottom for oil below the machinery, and bunker oil was carried in small tanks in the engine-room. There was a large hook constructed as part of the stern of the ship, presumably for towing oil barges.

Within four years of their first steam-tanker Nobel Brothers owned a dozen oil-fired tankers on the Caspian and as many shallow-draft tank barges on the Volga, representing an investment of over £250,000. Six of the Caspian ships were of the *Koran* design, with two longitudinal bulkheads, and had engines of 120 nominal horse power driving them at 10 knots. Their bunkers held sufficient to last the round trip from Baku to the mouth of the Volga, taking six days. Capacities ranged from 750 to 800 tons of kerosine—the difference being caused by some of the vessels having small tanks abaft the cylindrical tanks.

British shipbuilding came go the fore in constructing Russian tankers about this time, and in 1883 Armstrong, Whitworth built three vessels—the *Massis*, a freighter with a midship tank holding about 70 tons; the *Poseidon*, a similar vessel, with McInture tanks as a double-bottom holding 300 tons of petroleum cargo (she had a pumping installation and pipes); and the *Armeniak*, which was the most important. While the other two were mainly case-oil carriers, this vessel was built essentially as a tanker, having no dry cargo space, but two main tanks with a centre-line division and two large cofferdams at either end. These were connected by pipe-lines to a steam pump on deck. The engines of all three of these vessels were *aft*.

Early in 1885 L. V. Sone of New York had patented a plan for "Improvements for Transportation of Liquid Cargoes in Bulk," and subsequently arranged the wooden barque *Crusader* in accordance with the patent. This consisted of three tiers of *horizontal* cylindrical tanks, forty-seven in number, placed in such a manner that each was located below a hatch, and each was installed so as to be independent of the others. A pipe was connected to each cylinder and passed up the hatchway above to be attached with flexible hosing for filling and emptying the tank. Another line connected with a pressure tank, which supplied any want due to leakage and served as an overflow tank for expansion. While quite successful, few other tankers have been constructed on these lines.

Apparently Heinrich Riedemann of the Deutsche Amerikanische Petroleum Gesellschaft was influenced by the *Crusader*, as he took the *Andromeda* and constructed seventy-two steel tanks as a part of her hull, twenty-four on each of the three decks. Each tank had its own pipe-line for loading and discharging, and there was a cistern for expansion, etc., on each deck. The filling pipes were connected to a main fore-and-aft pipe running along the centre-line to the pumps. When completed she held 3000 tons of oil.

The years 1885–1886 were very active and did a great deal in developing the tanker. The *Sviet*, built by Lindholmen's for the Russian Steam Navigation & Trading Company of Odessa, was a successful vessel of this period. She had a speed of 11 knots. Her engines were aft, and separated from the cargo space by a cofferdam constructed fore of the cross bunker. She was equipped with both longitudinal and transverse bulkheads. The walls of the oil compartments were built within the sides of the ship, and a space of nearly two feet was left between the top of the tanks and the upper deck; below them was a cellular bottom. An oil-tight steel plate formed two

GLUCKAUF, 1886.

tiers of compartments for the cargo. Expansion trunks were provided, and the 1700-ton cargo could be emptied in about five and a half hours by pumps in the bows. The pipe-lines ran along the space between the tanks and the hull, with branches enabling individual loading and unloading of the various tanks. The empty spaces were well ventilated, and no trouble was encountered with regard to leakage.

The *Bakuin* was considerably in advance of previous steamers of the converted type. The oil above her cellular bottom extended to the skin and up to the height of the tween-deck, where there were some smaller oil tanks. The latter did not extend to either side of the vessel or to the deck above, it being claimed that the immersion of the lower tanks prevented any appreciable rise in the temperature of the oil, and that the upper tanks did not reach such a high temperature as they would if they extended to the deck and sides. She had cofferdams on both ends of the oil tanks. An additional cofferdam amidships provided for the carriage of more than one type of product without danger of contamination. This was a definite advance. Valves for regulation of discharge were located in the engine-room aft. Cooking and heating were by steam, and electric lighting was fitted. All were precautions against fire, which was her ultimate fate. She was destroyed by fire in the floating dock at Callao Bay, Peru, in 1902.

Meanwhile Riedemann had arranged the construction of the *Gluckauf* to designs previously shown him by Colonel Henry F. Swan. These had been commenced in 1883, being based on those of the *Armeniak*. The *Gluckauf* was built under Bureau Veritas survey, and was the first tanker to have her midship section registered by any classification society as that of a "Petroleum Steamer." She was constructed by Armstrong, Whitworth with the usual centre-line and transverse bulkheads, with engine-room aft and separated from the cargo space by the pump-room—which formed a cofferdam. She had a fore-and-aft continuous trunkway which cared for expansion, lighter oil cargo being carried alongside. A double-bottom was provided only beneath the engine-room. The *Gluckauf* is accepted as being the prototype of the modern tanker. Her sister-ship, the *Vorwarts*, remained in service until July 1890, when she was lost at sea.

Another vessel launched almost simultaneously with the *Gluckauf* was the *Petrolea*. She was a pronounced departure from previous designs, for she had various features not embodied in other tankers, either at that time or since. She had proper bulkhead arrangements, to care for cargo movement, and these were strengthened by means of struts. Her side tanks were bounded by a peculiar arched roof. She was built by Lindholmen's for a subsidiary of Nobel's, and it is reported that one of her first trips was to bring a cargo of 1000 tons of petroleum from Libau to London.

The *Petriana* and *Chigwell* were converted for Alfred Suart and Company the same year, the conversion having been carried out by Hawthorn, Leslie and Company. The *Chigwell* was given seven tanks, four forward and three aft, the capacities ranging from 160 to 420 tons. Longitudinal bulkheads were provided and the pumps worked at the rate of nearly 200 tons per hour.

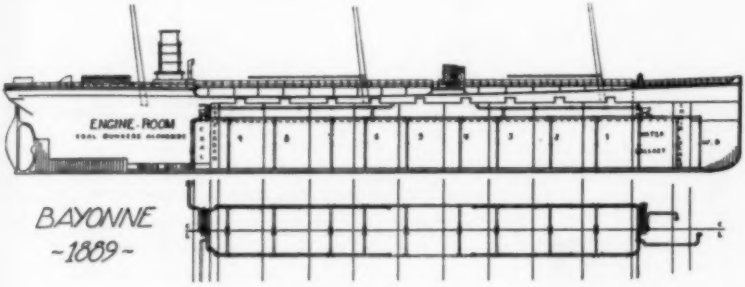
The *Petriana* was of similar construction, and in November of that year she brought the first cargo from Batoum to Liverpool under the command of Captain Davies, now partner in the well-known firm of Davies and New-

man. The run lasted eighteen days. (At the time Captain Davies was only 24 years of age.)

The *Charles Howard* was converted to a tanker in 1887, and was fitted to burn oil-fuel, which was carried in the double-bottom below her machinery space. Unfortunately, the oil-firing installation broke down on her maiden voyage and was removed in favour of coal.

The *Era* was built by Palmers, Hebburn & Company, to the order of Colonel Isenbeck, that year. Although not much larger than the average vessel of the period, she had thirteen bulkheads, giving great structural strength.

What is possibly the greatest weakness of the tanker is that while it will travel loaded one way, it must travel light on the return voyage. As a result, many vessels were constructed as dual-cargo ships, having extra-large hatches and being provided with windlasses and other necessary equipment allowing the employment of the vessel for general cargoes on the return voyage. Some vessels of this type have carried rare silks and spices without ill effect, and one carried a load of pianos.



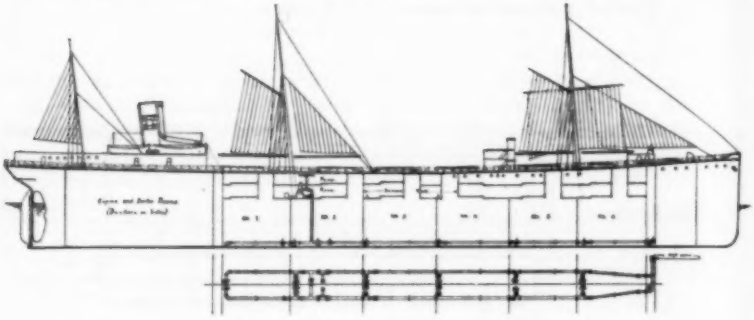
When Standard Oil entered the European market by means of the Anglo-American Oil Company in 1888, it bought outright about a dozen tankers, and when a year old had the *Bayonne* built by A. & J. Inglis, Ltd., of Glasgow. She conveyed petroleum from the U.S.A. to the company's depots at Bristol, Hull, Liverpool and London, her capacity being 4000 tons. The customary bulkhead arrangements divided her cargo space into eighteen compartments, at either end of which was a pump. These pumps were capable of emptying the cargo in ten hours. She had a loaded speed of 11·85 knots.

The *Christine* was built by Burmeister & Wain in 1890 for the Danske Petroleums Akiets., of Aahus, to the highest class Bureau Veritas. As well as a longitudinal bulkhead and transverse bulkheads, she obtained additional structural strength from six web-frames interspersed midway between each thwartship bulkhead, or about 24 feet apart. She also had a number of longitudinal stiffeners.

From the pump-room ran a double line of 6-inch pipe with two deck connections for loading and unloading. The *Christine*, which carried about 4000 tons of oil, later passed into the hands of the Anglo-American and was re-named the *Tioga*.

About this time many well-known authorities put forward the argument that all large tankers should have their engines amidships, since there was a great risk of straining a vessel with the larger cargoes that were then being carried, in cases where the engines were aft. This risk was increased when steaming in ballast in heavy weather. It was pointed out that having the engines amidships enabled the vessel to be more easily trimmed, more easily manœuvred, to be kept on a more even keel, to travel faster and to burn less fuel. For many years the arguments were so strongly in favour of this type of construction that it appeared that only smaller tankers would have engines aft, but the additional expense, involved through the necessity of constructing a shaft-tunnel, caused naval architects and engineers to redouble their efforts to discover some means of overcoming this problem.

However, a number of large tankers were still built with their engines aft. Among them was the *Turbo*, built by Sir James Laing & Sons of



TURBO, 1892.

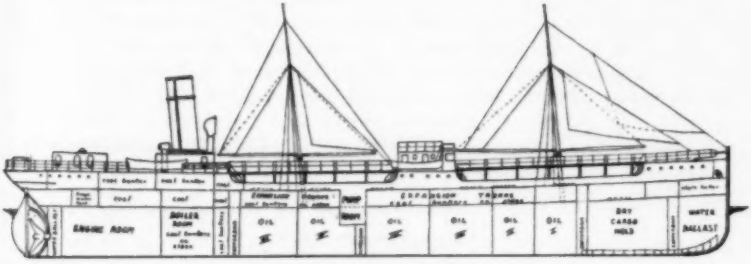
Sunderland for the Shell Trading & Transport Company in 1892. She had six main oil tanks with a total capacity of 4630 tons, but including the oil in her summer tank, expansion trunks and fore cofferdam she could carry 5125 tons. The pump-room was in the tween-decks abaft the summer tank. She had a double line of pipe with single suctions in each tank, cross-over lines being provided in the pump-room, tank 2 and in the fore cofferdam. She broke her back at Niewe Diep in 1908.

Prior to this date great opposition had been met with by tanker owners who desired to dispatch their vessels through the Suez Canal, owing to the alleged danger to other shipping in the limited waterway, but in this year the objections were finally over-ruled, and the *Murex*, specially built for the purpose, was towed through the canal with a cargo of bulk oil. She had large cofferdams, or water ballast-tanks, between her cargo tanks, which were employed in the same manner as those of the modern tanker passing through the passage. They were filled with water before entering the canal, so that should the vessel go aground she might be lightened by pumping out the water rather than oil. All tankers built since have embodied this principle, although nowadays on a somewhat modified scale,

and of course tankships are now permitted to pass through under their own power.

The *Potomac* was a record-breaker in her day. She was the "crack" tanker, not only of the Anglo-American fleet, but of the world, having a loaded speed of over 13 knots—slightly higher than the average speed (light) to-day. In her first ten years of service she made two hundred crossings of the Atlantic, and travelled almost a million miles. She was wrecked and abandoned in the Bahamas in 1929, after thirty-six years of continuous service. Her design and construction were similar to those of the *Bayonne*, and she was built by the same firm, in 1893. She had a capacity of 5300 tons—considerably more than that of the other vessel. She was a remarkably fine sea boat and an economical and safe oil-carrier. On her maiden voyage the *Potomac* discharged the first cargo of bulk-oil at Dublin, 1,206,200 gallons of illuminating oil.

While there had been at least one previous attempt to employ oil-firing in ocean-going tankers, the first oil-burning tankship in continuous sea service was the *Baku Standard*, built in 1894 by Armstrong, Whitworth for the European Petroleum Company.



CZAR NICOLAI II, 1895.

The *Czar Nicolai II* was launched the same year by F. Schichau G.m.b.H. of Danzig, having been constructed for Mineraloelwerke, Albrecht & Company of Hamburg, with a capacity of about 2100 tons. She had six tanks for the oil, separated abaft tank 4 by the pump-room and a cofferdam.

The *George Loomis* is an example of the small coastal tanker used on the Pacific at this time. She was built by the Bethlehem Shipbuilding Corporation, Ltd., San Francisco, in 1896 for the Pacific Coast Oil Co. She carried 800 tons of oil. Her cargo space was divided by one centre-line longitudinal and two transverse bulkheads. She had a single line of pipe connected with each tank and the three cofferdams. Her ultimate fate was to be lost at sea without survivors.

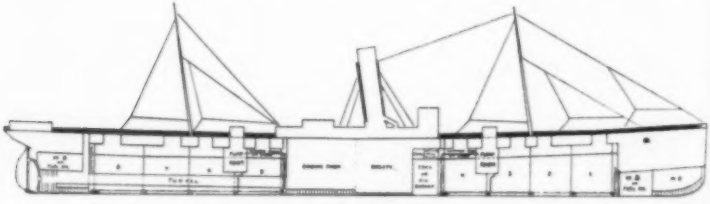
The first twin-screw steam tanker seems to have been built by Lindholmen's in 1897 on behalf of Ali Abas Dadascheff of Baku. She was the *Assan Dadascheff*, and had her engines amidships, with three tanks forward and two aft. By this time it had become customary to have the pump-room serving either as a cofferdam or placed in the tween decks, but she had hers on the deck. Her piping arrangements were such that tanks might be individually loaded and unloaded.

The sister-ships *Syriam* and *Kokine* were built for the Burmah Oil

Company for the Indian trade in 1899, embodying a number of interesting features. As well as the oil compartments, they were also constructed with holds for case-oil, or general cargo, and were fitted with portable ceiling and sparring. They were equipped with arrangements for dispelling vapours and extinguishing fire by means of steam passed through the pipe-lines. All valves were controlled from the pump-room.

Nobel's seem to have captured the honour of being the first to introduce the operation of Diesel-driven tankers. The best known of their early ships of this type were the *Vandal* and the *Sarmat*, put in active service in 1903. They each carried 750 tons of refined products from Rybinsk to St. Petersburg by way of the Volga and canal systems. Each was propelled by three Diesel engines of 120 horse-power each. As their engines were amidships, electric transmission of power was employed between the two compartments, thus not interfering with the construction of the intervening oil tanks. This seems to be the first instance of diesel-electric drive, still not fully developed to-day.

The *Narragansett* now considered to have been before her time, was built that same year for the Anglo-American by Scott's Shipbuilding &



NARRAGANSETT, 1903.

Engineering Co. and was about twice the size of any previous tanker. She held the record of being the largest until about the beginning of the World War. Her tremendous size made necessary the construction of midship engine arrangements and the building of a circular shaft-tunnel through eight separate oil compartments astern. There were also eight tanks forward and four smaller summer tanks. She had a pump-room fore and another abaft the machinery space, and her four pumps were capable of discharging the entire cargo in twelve hours, or at the rate of 900 tons per hour. She was equipped with numerous large cowl ventilators and had special derricks and winches, so that she might also be used for dry cargo if necessary.

The *Narragansett* was driven by a set of massive triple-expansion engines with a speed of over 13 knots. Her average speed with a full cargo was 11·5 knots, with a coal consumption of 49 lb. per 1000 ton-miles deadweight, which was considered to be a very satisfactory performance. This well-known vessel's career ended during the World War, when she was torpedoed and sunk by an enemy submarine off the Scilly Islands, March 16, 1917. No trace was found of the officers or crew.

In 1905, the *Colonel Drake* set up a record by towing the first ocean oil-barge across the Atlantic. This method of petroleum transport was

already very popular on both the Atlantic and Pacific seaboards of the United States, some vessels going as far as Japan in this manner.

A famous pair of vessels in the service of the Anglo-American were the *Iraquois* and the *Navahoe*. The former was the first tanker to be built with twin-screw engines *placed aft*, and was designed to tow the six-masted, schooner-rigged barge *Navahoe*. Between them they carried 18,000 tons of oil, and made successful voyages together up to a few years ago. Two towing lines were always used at sea, and due to a special device, the cable was rarely parted.

The tank-steamer *Paul Paix* inaugurated an entirely new principle of tanker construction, being the first ship constructed on the Isherwood longitudinal system of framing. In this system the closely-spaced transverse ribs that appear in the construction of an ordinary vessel are omitted. The transverse strength is obtained by fitting a series of strong transverses at widely-spaced intervals. These extend completely around the sides, bottom and deck of the ship, and are slotted to allow longitudinal frames and beams to be fitted continuously from bulkhead to bulkhead. The Isherwood system is of particular advantage in tankers, as it gives greater strength with increased deadweight capacity and yet requires less material. Although the engines of the *Paul Paix* were amidships, it has been this system that has enabled the machinery of large tankers to be placed aft.

The *Vulcanus*, 1194 tons deadweight, was the first ocean-going diesel tanker and the first sea-going motorship to receive Lloyd's classification. She was built to the order of Sir Henry Deterding in 1910, with a 400-h.p. Werkspoor engine, which gave her a speed of 8 knots on $1\frac{3}{4}$ tons of fuel per day. She served in the Anglo-Saxon fleet until December 1931, when she was broken up. Her engine was said to be in perfect running order after propelling the ship about 1,000,000 miles.

Scarcity of tankers during the War lead to many cargo vessels being converted and various different forms of construction attempted. One of the designs brought forward during the War was the so-called "Standard" type tankship, which was constructed with the machinery amidships to enable an easy re-conversion to ordinary cargo at the end of the War. Due to risk of loss through enemy action, scarcity of raw materials, and to save time in construction, no material was put into them that was not absolutely necessary. Some of these vessels are still operating at the present day.

This type had three cargo tanks forward and three aft. Since fewer bulkheads were used, the compartments were somewhat larger than those of the ordinary tanker. A single 10-inch pipe-line ran fore and aft with a single suction in each tank. As the main line passes through the boiler room, engine-room, etc., this type of vessel is not suitable for carriage of volatile products due to danger of gas leakage. These vessels have no summer tanks or expansion trunks, the hatches being about three feet deep. Those which were converted have, of course, double-bottoms. Other converted vessels had cylindrical tanks, but few of these were similar in arrangement.

Another type of tanker built during this period employed cylindrical tanks in order that the vessels might be converted to ordinary cargo carriers after the War was over. Among them was the *Aztec*, which was designed

with an ordinary hull with cellular bottom and had vertical cylindrical tanks which were nearly the same diameter as the beam at the particular spot at which they were constructed. These were connected by trunking on the deck, and the exposed trunks were divided thwartships at each tank, keeping them distinct.

The tanks were attached to the shell of the ship by steel webs in such a manner that each formed a semi-circular bulkhead across the vessel. The spaces between accommodated the pumps, pipes and valves. There was an oil-tight central longitudinal bulkhead between the tanks. Transverse bulkheads, which were not oil-tight, were fitted internally in each, and were connected to the webs on either side. However, it was generally recognized that the disadvantages of this type of vessel outweighed the advantages, with the exception of very specialized fields.

Many tankers were lost during the War, and Britain was short of oil. At the suggestion of the late Sir Marcus Samuel, and to the details worked out by Cornelius Zulver, the double-bottoms and ballast tanks of many liners were prepared to carry oil. Starting at the end of June 1917, 831 ships were fitted out in the United States and 430 in the United Kingdom, transporting 1,014,570 tons by the end of the War. Of this 15,191 tons was lost through enemy action and 2201 tons through marine casualties.

Of particular interest among the United States naval tankers is the *Patoka*, built by the Newport News Shipbuilding & Dry Dock Co. in 1919. Under navy classification she is designated as an auxiliary oiler, but is fitted with a special mooring mast to act as a tender for dirigibles and other lighter-than-air craft.

Propulsion is by means of reciprocating, vertical, quadruple-expansion engine, three single-ended fire-tube boilers and one auxiliary boiler. The total indicated horse power is 2917 and she had a trial speed of 10·87 knots. Accommodation is provided for 28 officers and 138 men, while for defence she is furnished with two 5-inch guns. The *Patoka* has operated continuously in the Navy in the Pacific, European and Turkish waters as tender for airships.

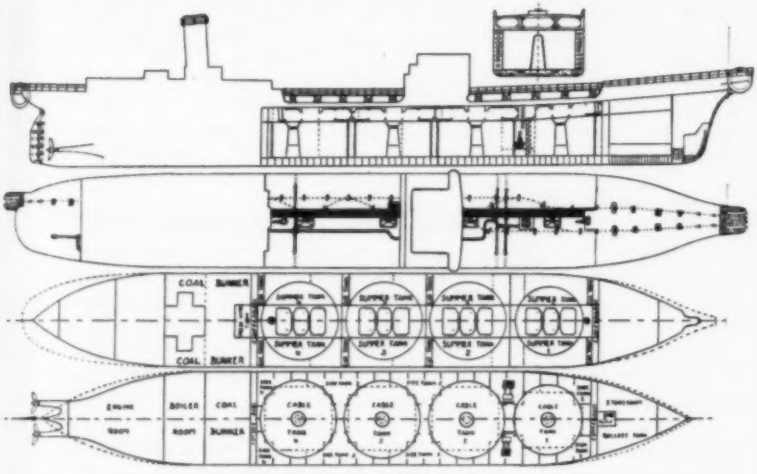
The weakness of tankers, as has been mentioned before, lies in the fact that most tankers can carry but liquid products. To overcome this fault a number of combination oil-and-ore carriers were constructed in the United States by the Bethlehem Shipbuilding Co. for the International Petroleum Co. and the Ore Steamship Corp. One of these, the *Charles G. Black* (ex *G. Harrison Smith*), was built in 1921. Her ore-holds occupy a fore-and-aft length of 360 feet, divided into three compartments and surrounded by the oil tanks. The oil space is divided into eleven tanks, subdivided longitudinally by a centre-line bulkhead. The expansion trunks are formed by the space on either side of the ore-hold. She has a total capacity of 18,500 tons of oil cargo, and the pipe-lines are on the deck, one on either side. She carries oil from Mexico to South America and returns to the U.S.A. with ore.

With the increased demand for natural gasoline large enough quantities became available for transportation by tanker; so the Standard Shipping Co. made a thorough investigation to determine the practicability of handling this product with safety and minimum loss in transit. As a result the *S. B. Hunt* and *W. J. Hanna*, built in 1919 and 1920 respectively, were specially

equipped for the carriage of this product. The two principal features of the system used consist of a gas-salvaging and a water-cooling system which may be applied to any one of the vessel's tanks in which the high-test cargo is carried under pressure. Experience has shown that this type of cargo can be done with exceedingly small losses and with entire safety.

The Norwegian tank steamer *Arthur W. Sewall* was built by Sir W. G. Armstrong, Whitworth & Co., Ltd., under an agreement dated April 18, 1925, made between a Norwegian company, A/S Ivarens Rederi, of Oslo, as owners, and The Barber Asphalt Co. as time charterer. She was delivered May 7th, 1926, and is still in operation, the charter having been extended.

Her particular interest is that she was designed to carry heavy oils, having a capacity of 60,000 brl. of 17° Baumé crude oil (0·952 sp. gr.), but with minor exceptions does not differ from the ordinary tanker in respect



NEPTUN, 1926.

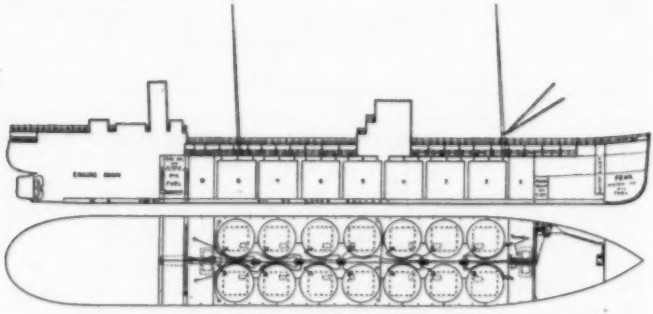
to general appearance. The most important feature is that her cargo tanks are fitted with a greater steam coil-heating capacity than would be required for normal crude oil, and her pumping equipment is designed to handle crude oil as heavy as 8° Baumé (1·059 sp. gr.). She is accordingly equipped with excess boiler capacity to harmonize with the larger pumps and additional heating coils. The main suction pipe-line is of 18-inch bore, and the heating coils are of 2-inch bore with ½-inch walls. Taking tank 6 as an example : tank capacity, both sides, 1435 tons; heating surface, 2 square feet per ton; total heating surface, 2870 square feet. All told, there are 4384 feet of heating coils in tank No. 6 alone.

The *Arthur W. Sewall* was primarily intended, at the time of the agreement, to haul very heavy asphaltic oil from the property of The Bermudez Co. in Eastern Venezuela, which oil in order to be moved had to be heated to 190° F. for loading and discharging. This was successfully done with her equipment.

Since The Barber Asphalt Co. has become dissociated from The Bermudez Co., in Eastern Venezuela, the vessel is now being for the most part used in hauling Venezuelan oil from Curaçao to New York.

Another variation in design is found in the *Neptun*, which was built in 1926 by Blohm & Voss, Hamburg, for the Norddeutsche Seekabelwerke, Aktiengesellschaft, of Nordenham. She is a combination cable-ship and tanker, being built to the Isherwood longitudinal system. Oil is carried in her four cylindrical tanks, and in the side tanks formed between the cable tanks and the hull. In the centre of each of the cylinders is a cone, round which is wound the cable. The side tanks number four, and are divided *between* the cylinders by a centre-line bulkhead. She also has summer tanks on either side of the expansion trunk. Her speed is 11 knots, she will carry 10,033 tons of oil and her cable capacity is 8000 tons. She is equipped to carry naphtha and has heater coils for heavy gravity oil.

The *General Gassouin*, built for the Standard Oil Co. of New Jersey, was specially designed to transport motor oils of various grades. She was



GENERAL GASSOUIN, 1927.

constructed to the Isherwood longitudinal system by Forges & Chantiers de la Gironde, with her engines aft in the conventional manner. However, her outward appearance does not tell all, as the greater part of her cargo is carried in fourteen cylindrical tanks, arranged in two rows. Oil is also carried in two pairs of tanks fore and aft of the circular tanks. She carries a total of about 5465 tons of oil. Her double bottom may be employed for either water ballast or further oil cargo. Bunker tanks, isolated by cofferdams, are situated abaft the cargo tanks. Each tank has an individual expansion trunk between the top and the deck above.

There are five pumping installations for loading and discharging the oil, each handling four tanks, except the last, which cares for only two cargo tanks, also the cofferdam and double bottom. A complicated system of cross-over lines, etc., has been arranged to give complete flexibility in handling cargoes, permitting practically no possibility of contamination by other grades of oil, or by water and/or moisture. As the cylindrical tanks are not in contact with water, there is no deterioration of the lubricating oil due to "sweating" of tanks. The *General Gassouin* is still in transoceanic service between France and the United States.

The Isherwood Bracketless system was introduced about this time. This system removes the points of greatest stress—which are at the bracket connections around the bulkheads—by fitting the deep transverse frames closer to the bulkheads. For comparative purposes the longitudinals may be considered as *fixed* at the transverses and *supported only* at the bulkheads. The maximum stresses on the longitudinals are now transmitted to the deep transverse frames, and the stresses on the longitudinals at the bulkheads are reduced to a minimum.

Continuity of the longitudinals is insured by fitting shell doublings or wide liners in the vicinity of the bulkheads. These are fitted in way of every strake on the bottom and alternate strakes on the sides and deck.

No saving in weight is claimed, as actually there is a slight increase, but the system gives reduced cost of upkeep, damage repairs, and cleaning. It also decreases damage, labour constructional cost and gives greater rapidity of construction.

The first tankship to employ the Bracketless system was the *British Inventor*, built by Palmers Hebburn Co., Ltd., for the British Tanker Co.

The tanker *Brunswick*, built by Scott's Shipbuilding & Engineering Co., Ltd., Greenock, for the Atlantic Refining Co., in 1928, aroused keen interest in marine engineering circles because of the new features which her design embodies. She was the first diesel-electric driven vessel built in England, and the largest afloat. Owing to the use of standardized land-type non-reversible oil engines and standard electrical equipment, together with the smaller auxiliaries required, the whole cost of the machinery equipment was not more than that of a direct-driven motor tanker designed to carry the same amount of cargo. She was the ninth electrically propelled vessel to be added to her owner's fleet (their first such vessel being the *J. W. Van Dyke*, which was the old *Allentown* converted to diesel-electric drive). Her main accommodation and bridge are aft, and the usual funnel is omitted because the only uptakes are those of the auxiliary heating boiler, the four exhaust pipes and silencing heads for the generator engines.

She is framed on the longitudinal system, and has ten pairs of main and summer tanks, all of which are fitted for the carriage of volatile products.

The *Brunswick* is driven by a single-screw motor, to which power is supplied by four Ingersoll–Rand type, four-stroke engines, working on the airless injection principle. Each of these is coupled direct to a d.c. propelling generator and to an auxiliary generator arranged in tandem, which supply power to the ship's auxiliaries and excite the fields of the main generators and the propelling motor. The motor generators and all electrical equipment were supplied by the British Thomson-Houston Co., Ltd. As the propelling motor is really *two motors connected in series*, it is possible, when only using one-half of the motor, to develop sufficient power for three-quarter speed. By varying or reversing the excitation in the main generators, it is possible to start, stop, and reverse the main propelling motor. On trial she developed 11·48 knots.

The design of the marine engine is one that, with slight alterations by the builders, had already proved successful in the earlier vessels of the Atlantic Refining Co.

The main switchboard, which is at the main deck level over the engines, comprises eleven panels having an over-all length of 30 feet. There is

one motor control panel and four generator panels—which *put in* or *take out* from circuit the four generator sets. Earth detector voltmeters and earth detector lights are provided, and there is a complete series of mechanical inter-locks, which are designed to prevent careless handling of switchboard arrangements. These ships do not carry electricians or special electrical engineers, and it is said that "the only duty of the engineers is to keep the electrical apparatus clean," which policy is found quite satisfactory by the owners.

The *Brunswick* returned with her first cargo of light oil to Thameshaven in October the same year, performance having proved satisfactory under service conditions. Her capacity is 110,961 barrels.

The twin-screw *Megara*, built for the Royal Dutch-Shell interests, was the forerunner of a great many similarly propelled tankers. Her particular interest is that she was equipped with continuous supercharged diesel engines, which give about 40 per cent. increase in power with no increase in weight or size. This system was worked out by Cornelius Zulver in collaboration with Werkspoor's. The *Megara* travels at 13 knots light and 12·5 knots loaded.

Reviewing the period from 1931 to the present date it is noticeable as being among the most active of any similar period during the history of the tankship. Among other records, that of *speed* has been continually broken by the Japanese. In 1931 the *Teiyo Maru* was built for the Nippon Tanker Co., and attained 17·53 knots light and 16·74 loaded. She is propelled by Yokohama-M.A.N. two-cycle, airless-injection diesels, has a large pumping plant consisting of four simplex steam pumps with a capacity of 8400 brl. per hour, and three steam boilers for power. Her cargo capacity is about 12,000 tons.

The *Agnita* so-called "mystery-boat" of the Royal Dutch-Shell interests, was built to carry 4600 tons deadweight and is arranged to carry propane and sulphuric acid in domed, vertical, cylindrical tanks, and gas-oil in the spaces between. There are six tanks on each side of the longitudinal bulkhead, and the domes project slightly above the level of the deck. Acid is conveyed from Europe to Curaçao, where she may load gas-oil both inside and out of the circular tanks, or alternatively, load with gas-oil *outside only* and proceed to Port Arthur for a cargo of propane for her cylindrical tanks. Her construction is such that she can carry a full cargo with either oil or special cargo in her tanks. Provision was made so that the cargo in the cylindrical tanks can be carried under pressure, and actually unload itself. No trouble is experienced with the acid, as it is highly concentrated, and will not react with the metal so long as no water or moisture is permitted in the tanks. She accommodates twelve passengers. Propulsion is by means of a Werkspoor, 4-cycle, double-acting, continuously supercharged diesel, the speed being from 12·5 to 13 knots.

The sister-ships *Mijdrecht* and *Moordrecht* were also built in the same year for the Van Ommeren interests, and constructed on the Isherwood system. Each has a capacity of 10,130 tons, and they are of particular interest because they were among the first tankers to have a stream-lined superstructure. (The 11-knot diesel-tanker *Katendrecht*, built in 1925 for the same concern, was probably the first tankship to which stream-lining was ever applied.)

Their hulls were both divided into twenty-one cargo tanks, with the pump-room between tanks 4 and 5. When these vessels were launched it was still not quite understood, in general tankshipping circles, as to how stream-lining would give them any particular advantage over the more orthodox design. It was felt that, if the tankers were high-speed units, the reduction in wind resistance would be worth while, but not in the case of a relatively slow-speed ship.

The sister-ships *Virginia Sinclair* and *Harry F. Sinclair, Jr.* were put in service by the Consolidated Oil Corporation late in 1930 and early in 1931 respectively. They were built on the Isherwood system with double-longitudinal bulkheads, and were designed primarily for carriage of casing-head gasoline, the usual summer tanks being replaced by a complete water-sprinkling outfit covering the entire deck. The tanks are capable of withstanding the high-pressure necessary for carrying high-test, and are arranged so that up to seven grades of refined oil may be carried without risk of contamination. Each vessel carries 67,000 brl. They were built by the Bethlehem Shipbuilding Corporation, Ltd., with double reaction turbines of 400 lb. pressure. Three water-tube boilers with 200° of super-heat were adopted, enabling a loaded sea-speed of 14 knots to be attained.

Of the tankers constructed between August 1933 and June 1935, the largest number ordered by any single group was that of the Royal Dutch-Shell, about thirty vessels, most of which were around 11,000 tons dead-weight. The Standard Oil interests ordered a number of 15,000 tonners, and since the latter date both groups have placed several more tanker orders.

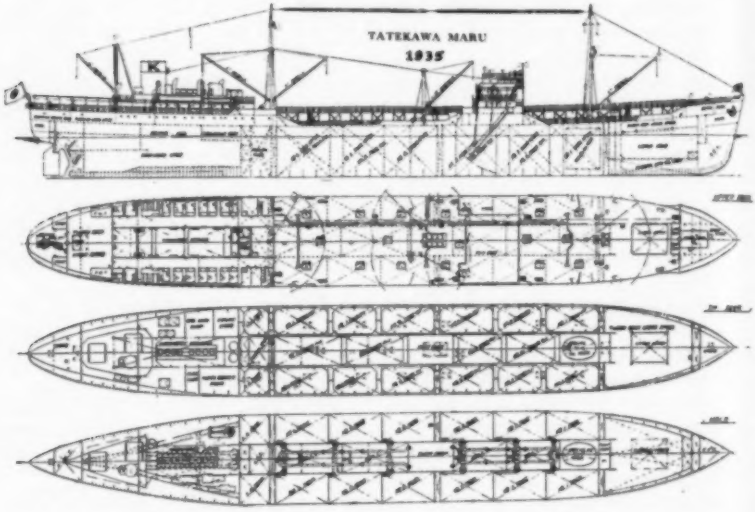
Two 12,300-ton vessels, the *Grena* and *Brajara*, were completed at the end of 1934, both having stream-lined deck erections, resulting in a 40 per cent. reduction in air resistance (with a wind of 15 metres per second) representing a saving of about 7 per cent., or about 1 ton of fuel per day.

These ships have two longitudinal bulkheads and continuous longitudinal girders. Bunkers are carried forward of the machinery space, with reserves below the dry cargo hold forward. The respective loaded trial speeds of the two vessels were 12·62 and 12·75 knots.

Japan is the only nation which has shown any inclination either to build for its navy, or to support owners who are willing to build, fast special tankers for naval work. The oil-carrying motor ships that have been built in Japan during the past few years have all broken speed records set by their predecessors. The *Fujisan Maru* made 18·8 knots, the *Toa Maru* attained 19·25 knots, and in 1935 the *Tatekawa Maru* established a record of 20·5 knots. There is also the 18-knot service-speed ship *Kyokuto Maru*. The latter, built without any assistance under the " New Construction Facilities Act," is 13,691 tons deadweight, and is one of the highest-powered single-screw motor ships in existence. Besides her 14,599-cubic-metre heavy-oil capacity and 277-cubic-metre special-oil capacity, she has a hold for carriage of silk, and a dry cargo hold forward. She has two longitudinal bulkheads, and transverse bulkheads subdivide her oil space into six wing tanks on either side and five tanks and the special tank in the centre. The pump-room, in which there are four heavy-oil pumps and one for gasoline, is amidships. Two lines of pipe are laid to the oil tanks, with cross-over suction branches to each.

The *Moira*, constructed in 1935, is one of the largest all-welded tankers ever built, having a deadweight capacity of about 2240 tons. She is propelled by steam engines aft and is fitted to burn either coal or oil-fuel, her speed loaded being 10 knots. The machinery is separated from the cargo tanks by a cross bunker and cofferdam, and the oil is carried in five main compartments sub-divided by a centre-line and several thwartship bulkheads. The pumps, between tanks 3 and 4, have a total capacity of 400 tons per hour.

Another important vessel built last year is the *G. S. Walden*, the first tanker to be built to the Isherwood Arc-Form of hull construction, which was applied in conjunction with the Isherwood Bracketless system of framing. For purposes of comparison the Standard Transportation Co.



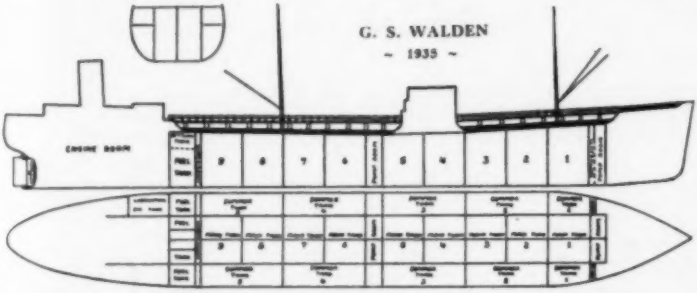
also had the *W. B. Walker* constructed to carry the same deadweight tonnage on an equal draft. Although the vessels are of equal length, the beam of the Arc-Form ship is nearly 7 feet greater than that of the other. Both are diesel-propelled, and although designed for a speed of 12·5 knots loaded, the Arc-Form vessel is stated to have developed one-half knot more than the other.

The principal idea of the Arc-Form design is to reduce the resistance which must exist by reason of the sharp, box-like bilge of modern ships. That resistance really exists has been proven by model experiments and also in practice. In order to obtain this fining of the bilge without reducing the displacement, or filling out the ends, it is necessary to keep the same midship areas as in the comparative, orthodox-form, vessel. This is accomplished by replacing the area lost at the lower water lines by an equivalent area at the upper water lines, requiring an increase in the ship's breadth in that region. This increase may be 5, 10, or 15 per cent., or any

intermediate percentage. Isherwood's consider that for general purposes the best *all-round* result will be obtained with 10 per cent. Arc-Form, as employed in the *G. S. Walden*. It is certain that the performance of that vessel has been highly satisfactory, because an order for a sister-ship was placed by the same firm soon after the trials.

Experiments on models with 7 per cent. Arc-Form have also shown very good results, and the Federal Shipbuilding Co., Kearny, N.J., commenced building two 12,500-ton tankers with 7 per cent. Arc-Form on its own account, these being purchased while under construction by Jersey Standard interests, and named the *R. P. Resor* and the *T. C. McCobb*. The Gulf Oil Corporation is having two 11,000-ton Arc-Form ships built at the Sun Shipbuilding Co.'s Yard, and two sister ships to the *R. P. Resor* have been ordered by the Pan-American Oil Co. The General Petroleum Co., California, is to place orders for two 15,000-ton tankships, and is considering this new hull design.

In about the middle of 1935 the motor tanker *Sheherazade* was launched in France, being the largest vessel of the year and by far the largest tank-



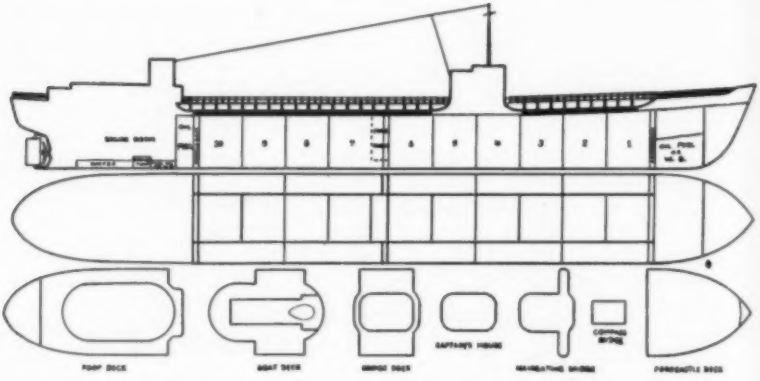
ship yet built in that country, having a cargo oil capacity of 18,500 tons. While her designed maximum speed is 14 knots, her cruising speed is but 12·5 knots. She also is the first large tanker constructed in France according to the Isherwood Bracketless system, and has two longitudinal bulkheads, with nine tanks located centrally and nine wing tanks on either side. Her pump-room is between tanks 5 and 6, with two steam pumps, each of 500 *tons per hour* capacity. She is equipped with cargo heating coils.

The *Sheherazade* was designed especially for the carriage of Iraq crude from the I.P.C. pipe-line terminal at Tripoli to Marseilles. Her owners are the Compagnie Auxiliare de Navigation, Paris.

An important tanker, the *Comanchee*, was recently completed for the Anglo-American Oil Co. with a designed deadweight of 10,200 tons, and a speed of 13 knots. She had been specially built for carriage of a large number of different grade lubricating oils, having twenty-seven compartments. The eight cargo pumps are of the rotary type, driven by condensed steam-engines. In order to avoid loading water ballast in the cargo tanks, the vessel has been built with a very deep double-bottom, a principle not used *deliberately* for many years. The ballast tanks will have a capacity of 3000 tons. Due to this design, an extra weight of 700 tons is involved in

the hull, but this sacrifice was considered worth while because of the advantages accruing to it. The *Comanchee* is in keeping with Standard Oil's periodic efforts to evolve the most efficient means of lubricating oil transport, previous boats having been notably the *General Gassouin* and the *Hanseat* (the latter was built in 1929 to somewhat similar design as the former).

The *Mosli*, 12,500 tons d.w., which was completed in 1935, was the first tankship to be built with the Maierform hull. Since her design is otherwise mundane, this only will be dealt with. The Maierform may be most aptly visualized by picturing a tanker with a hull shaped like that of a racing sail-yacht, without a keel. This gives a somewhat increased breadth and capacity, and more buoyancy in the bows. Other advantages claimed are: reduction of pitching, especially in a head sea, and consequently an increase in average speed, as the propeller does not emerge so frequently as with a normal hull; less water is taken on the forecastle in heavy weather; easy



MODERN MAIERFORM TANKER WITH STREAM-LINED SUPERSTRUCTURE.

maintenance of course; less resistance; and manœuvring is easier in narrow waters and when the ship is in bad trim.

The two latest tankers being built with stream-lined deck erections are for Camilio Eitzen & Co., and Ludv. E. Braathen of Oslo. They embody the Maierform, and will be the largest to which stream-lining has yet been applied, having a dead weight of 14,500 tons capacity and being designed for a loaded trial speed of 13 knots. (To-day there are ten large motor tankers afloat and under construction, with stream-lined superstructure.) These two will have their cargo tanks divided by two longitudinal bulkheads, and transverse bulkheads to further divide the cargo space into ten main tanks and five wing tanks on either side. A saving in weight, other than that obtained by stream-lining the superstructure, is made by employing electric welding on a larger scale than in any other vessels of corresponding size, adding to the interest from another viewpoint.

The 2400-ton fruit and cargo carrier *Svanefjell*, completed recently for Olsen & Ugelstad, Oslo, is a throwback to the ships of sixty years ago, inasmuch as she is also provided with a deep tank to carry 300 tons of oil

cargo. It is understood that there are quite a number of vessels so fitted to-day.

Among the many other types of modern vessel, now in service, with which it is impossible to deal with more fully, are the shallow-draft ships on Central American rivers propelled with aerial propellers; and in China special ships with torpedo-boat destroyer engines, taking steam from water-tube boilers, navigating rapid rivers such as the Yangtze Kiang.

During 1936, four more high-speed tankers of 12,000 tons net cargo capacity will be completed in Japanese yards, making a fleet of eight vessels with speeds ranging from 17·5 to 20 knots, completing the present naval programme, and also one vessel of 15 knots service speed (*San Ramon Maru*). The first of the new vessels is to be put in service about May of the current year; her name will be *Otawa San Maru*.

According to figures given by important tankship authorities, 44 per cent. of the world's steam-tanker tonnage is over 15 years of age (the average life of a tanker), while 85 per cent. is over 10 years of age. It is estimated that during the next five years it will be necessary to build some 750,000 tons of tank vessels per annum, in order to meet requirements. The majority of this new tanker tonnage will of a necessity be placed by American firms, who own most of the obsolete and unserviceable tonnage.

It will be interesting to watch the form this construction will take. A review of construction during the past few years will show that the installation of two or three longitudinal bulkheads seems to be coming very much into favour. Electrically-welded construction is being used to a far greater extent; speeds are increasing; there is the question of streamlining, which has many advocates; and more vessels are being built for special-cargo purposes. Newer factors are the increasing attention paid to patent hull formation, such as the Arc-Form and Maierform, to give increased speed with less resistance and with greater carrying capacity and a diminished charge upon the fuel required per diem. Bow lines and stern design are also meeting with more consideration, and rudder forms and special propellers are used to an increasing extent. Cargo-pumping rates are also being speeded up. With regard to methods of propulsion, there is the slow increase in the use of the turbo-drive, diesel-electric drive and *perhaps even more so* the extensive use of super-charging.

As to the Isherwood systems, of the total 2000 ships built to them, aggregating 16,000,000 tons d.w. carrying capacity, 1040, or over 50 per cent., are tankers in service totalling 9,750,000 tons d.w. carrying capacity. Seven of fourteen under construction are Arc-Form.

The success of the new Anglo-Saxon tankships is largely due to the self-containedness of their main engine rooms and the fact that all the auxiliary machinery can be operated from the exhaust gas of the main engine, while the ship is at sea. The Anglo-Saxon fleet keeps not only to the 4-cycle system of operation but to the Werkspoor diesel engine, which has characterized the fleet since the building of the *Vulcanus* a quarter of a century ago. Should the company decide to have some of their future vessels designed for greater speeds, it will be interesting to note whether they retain the 4-cycle system or change over to the 2-cycle system as effected by the high-speed Japanese tankers.

Another fine fleet, which has contributed largely to the development of

the modern tanker is that of the British Tanker Co. (Anglo-Iranian). Twenty-five of the thirty-seven vessels, aggregating about 363,119 tons d.w., which were built to this firm's order between 1920 and 1925 employed double reduction geared turbines, from which considerable experience was gained. Thirty-five more ships were built during the ensuing five years, twenty-five of which were diesel-propelled. Now the company is building a further six 12,250 ton d.w. tankers, all of which are diesel-propelled.

Future construction will be influenced by all these factors. Speed may or may not be controlled by naval considerations, size by the proximity of field and refinery and by the lengths of voyages. Automatic equipment for navigation is also being improved and is becoming part of the standard equipment used, and the quick turn-round has evolved luxury accommodation for officers and crew.

More especially is there the desire for greater service speed—which will probably be raised to about 13 knots average. The United States Navy is particularly anxious for high-speed tankers but has not yet * obtained the necessary appropriations from Congress. In the event of war, the volume of tonnage it would have to pre-empt might seriously cripple the country's industrial oil movements. (Domestic water transport amounts to 51 per cent. of the total movement of petroleum and 26 per cent. of the crude oil movement.)

The speed of the commercial vessel would also constitute a hazard to the fleet. If it were faster moving, not only would fewer ships be needed, but they would also be safer. Utopia would possibly be approached by 18-knot tankers that could keep up with the rest of the fleet. It is a problem of economics—the Navy Department, which has not yet reached a conclusion *as to what these economics are*, is studying the question of what speeds could be built into ships as a compromise of the *ideal* and *practical*.

On the other hand, the matter, apart from the question of subsidies and naval requirements, might after all bear closer looking into by oil companies, in view of the results obtained by two of the Japanese 18-knot class ships. These have been making ten round trips to five or six by the conventional tanker, the result being that operating costs, including interest on the higher first cost, are reported to compare very favourably with the charges for four slower tankers necessary to provide the same service, apart from the feature of more rapid delivery, which has a financial value of its own not usually considered

It would be impossible, however desirable, to make separate acknowledgment of the obligations of which the author is aware. Nevertheless, sincere thanks are given to all those whose assistance and courtesy were so valuable. Of individuals, a few must be mentioned more expressly. K. J. Balsillie, Anglo-American Oil Co., Ltd.; A. L. Biggart, National Shipbuilders Security, Ltd.; Captain Davies, Davies & Newman, Ltd.; H. Flintoff, Sir Joseph W. Isherwood & Co., Ltd.; A. C. Hardy, International marine writer; Lieut.-Commdr. J. U. Lademan, Jr.; Bureau of Engineering, U.S. Navy; George Sell, Institution of Petroleum Technolo-

* Early in 1936 Senator Copeland introduced a bill before Congress which, if passed by both houses, will make available a subsidy of $5,000,000 per annum to aid the construction of 15- to 18-knot tankers on a basis of the higher the speed the greater the subsidy.

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A THEORETICAL EXAMINATION OF STRAIGHT-HOLE AND DIRECTED-DRILLING TECHNIQUE.*

By L. V. W. Clark, B.Sc., A.M.Inst.Mech.E. (Associate Member).

PART I.

Straight-Hole Drilling Technique.

It has been realized for a number of years that rotary-drilled holes have a tendency to deviate from the vertical, and many rules have been postulated to assist operators to drill straighter holes. The theory of straight-hole drilling is complicated by a number of factors, most of which are outside the control of the operator.

The great depths to which wells are now being drilled have meant an ever-increasing strength factor in all drilling equipment, and very much greater weights have now to be carried. Generally speaking, the improvements made in the surface equipment may be attributed to those increased loads, and the increased strengths of the various parts will have little, if any, effect on the problems encountered. In fact, any new ideas embodied in the surface equipment, with the possible exception of the slush pump and rotary table, can, so far as deviation of the hole is concerned, be completely ignored, and any improvements made can be assumed to assist only in the carrying of the abnormally heavy weights necessary for the deep wells now being drilled.

Minimizing lateral drift in sinking wells has increased considerably the cost of drilling and the time taken to reach the pay sand. Several factors exist to affect the rate of drilling. These are: (1) the design of the bit; (2) the condition of the bit; (3) the shearing resistance of the formation; (4) the jetting action of the mud; (5) the efficiency of circulation in removing cuttings from the hole; (6) the speed of rotation of the string; (7) the effective weight on the bit.

All these, with the exception of the shearing resistance of the formation, are under the operator's control, and can therefore be taken care of.

The development of drilling technique will depend on the ability to: (1) determine the fundamental causes of well deflections; (2) determine the best type of cutting tool to obtain the best hole-making performance; (3) develop straight-hole drilling technique which will be least prejudicial to high drilling rates.

The structural effects on deflections may be generalized as follows: (1) Both up-structure and down-structure deflections occur and are, approximately, equal in magnitude; (2) horizontal structures have no particular directional effect on deflections which occur, and it may be concluded that in a perfectly horizontal formation the bit would definitely take the vertical path as being the path of least resistance.

* Paper received January 14th, 1936.

These deflections are caused by the differential cutting and reaming action induced by the bit and changes in cutting quality of formations penetrated by the bit. It would appear that a distinct relationship is indicated between bore-hole deflections and the inclination and hardness of the formations penetrated.

Straight-hole drilling has been demanded for the following reasons: the difficulty of drilling, frequent fishing jobs and excessive trouble when the well is put on the pump due to wear on the tubing and rods, etc.

It was from these factors that operators began to realize that all was not as well at the bottom of the hole as was thought, and in 1927 efforts were made to determine the exact course of the hole. Instruments of the most ingenious kinds have been produced, but, even if the records which these instruments give be accepted, the operator is still faced with the problem of how to drill a vertical hole.

Results of experiments which have been published show little that has not already been discovered by those who have made a careful analysis of drilling conditions, and yet operators are constantly being urged to:

1. Ensure only a reasonable application of weight on the bit;
2. Ensure that the bit is correct to gauge and is sharp;
3. Keep a proper pump pressure;
4. Keep the drill pipe in tension by the use of a long heavy drill collar.

It may be assumed from a general survey of the results obtained from a theoretical examination of rotary drilling that, provided the weight on the bit does not exceed an amount sufficient to cause buckling, a reasonably straight hole may be expected. What this weight would be appears to be a matter of conjecture.

Turning to the theory that an increase in the weight of the drill collar and the bit will ensure a straight hole, it will be as well to examine this a little more carefully.

From the surface to the bit there is a varying amount of tension in the drill pipe, the maximum being at the surface and the minimum at the bit. If the pipe is suspended so that the bit is just clear of the bottom of the hole, and all the weight of the string is supported by the hook or is borne by the slips of the rotary table, the whole of the string will be in tension. Then the weight carried by the various portions of the string will vary with the depth, the maximum weight being carried at the surface and the minimum at the bit.

If the pipe is now lowered until the bit reaches bottom, permitting the bit to press into the formation an amount equivalent to the weight of the bit and drill collar, the amount of the weight carried by the portion of the string at the surface will be reduced by the amount corresponding to the weight of the bit and drill collar, and the weights carried by the portions of the string below the surface will be reduced by a similar amount. At the top of the drill collar there will be neither tension nor compression, since only the weight of the bit and drill collar has been removed.

It is obvious that a vertical axis cannot bend unless acted upon by external forces, if the axis is everywhere in tension. In a perfectly straight hole, then, a vertical axis will remain in that state so long as the conditions remain constant.

If now a further load is taken off the hook or table slips and more load is placed on the formation, the point of tension and compression travels further up the string. Since the drill pipe above the drill collar is of a much smaller diameter, the string will commence to flex or bend as soon as this point of tension and compression rises up the thin axis from the enlarged drill collar.

The amount of bending will be dependent on the size of the annular space between the hole and the pipe.

It is clear from this argument that a weight just slightly less than the weight of the bit and drill collar is the maximum weight that can be carried by the bit if flexing is not to occur. An obvious solution of the problem would therefore be to equip the string with a sufficiently heavy drill collar, and to increase the length and weight of this portion of the string to maintain a given ratio of weight per inch of cutting edge of the bit.

The problem propounded by this theory resolves itself into the question of accurately controlled bit pressure, and a uniform rate of feed whilst under accurate pressure control.

Uniform rate of feed of a rotary bit is necessary, as deviation of holes is often started when the bit is dropped into soft formations by the intermittent use of the brake during drilling.

How is the driller to know that he has no more weight on the bit than is required just to keep the whole string in tension? The weight indicator was invented to assist in the calculation, but unfortunately, due to extraneous forces, the weight shown on the gauge is merely an approximation, and only prevents the driller from putting on too great a weight.

The hydraulic rig has done a great deal to overcome this uncertainty, as the weight-indicating gauge can be calibrated directly against the hydraulic pressure required on the cylinders supporting the column of pipe. Even with this rig, however, certain factors must still exist to prevent the attainment of the perfectly straight hole.

The running of a bit not true to gauge or with a badly worn cutting edge will, of course, assist considerably in the deviation of the hole.

During the year 1929 investigations were carried out to ascertain the effect of varying the mud fluid pressures in the drill pipe. The hypothesis was that by maintaining a certain differential pressure above the bit the lower portion of the string would be put in tension, so that an increase in weight could be put on the bit before the string was placed in compression. This would enable hole to be made faster with safety.

Hayward [1] has dealt with this question, considering a 6⅝-inch string, the cross-sectional area of which, excluding the water-courses in the bit, is roughly 27 square inches. He considers an 11-inch bit, drill collar etc., and a mud fluid pressure of 290 lb. per square inch at the bit acting on the above-mentioned cross-sectional area. The effect of this intensive pressure would be to set up a tension of 10,000 lb. in the last joint of the drill pipe when the bit was off bottom. Thus a pressure of 10,000 lb. could be put on the bit without putting the drill pipe in compression.

With pressures ranging from 500 to 900 lb. per square inch at the pumps it would appear possible, using 6⅝-inch pipe, to drill to 5500 feet while maintaining some tension in the last joint of pipe, and yet to put a reasonable weight on the bit.

Assuming that it is possible and desirable to drill without putting compression in the lower end of the column of drill pipe, some effort should be made to maintain a maximum pressure on the bit. This can be done by making the holes through the tool joints as large as practical. In addition, the hole through the drill collar should be made the same size as that through the remainder of the drill string, in order that the pressure should be exerted directly at the bit. If the diameter of the drill pipe be enlarged somewhat for the lower 200 to 300 feet, greater weight could be applied to the bit without placing the drill stem in compression.

Large-size pipe with flush-jointed internal couplings for the bottom stands would appear to be the solution to this problem.

Hayward quotes as an example 6⅝-inch drill pipe with 7¾-inch couplings. If the lower 200 feet of the pipe be flush jointed with an internal diameter of 7 inches, it should be possible to put a weight of 13,000 lb. on the bit without putting any compression in the drill pipe, using a differential fluid pressure of 300 lb. per square inch and a bit and drill collar weighing 2200 lb.

The hypothesis put forward by Hayward has its disadvantages, one of which is difficult to overcome. The high differential fluid pressures have a detrimental effect on the upper end of the string, and the dead weight loads may be increased enormously. It will be necessary to decrease the additional tension in the pipe joints, due to the fluid pressure, and enable greater depths to be attained without increasing the total load on the joints, and at the same time maintain the straight-hole drilling effect of high differential fluid pressures at the bottom.

The study of the lowering and rotation of a long thin axis can be examined from another angle.

A string of drill pipe lowered into a hole can assume four main modes. Firstly, the string may be held freely suspended—that is, the lower end is not in contact with the formation below—and be stationary. Secondly, the string may be freely suspended at the surface, not in contact with the formation, and be rotating. Thirdly, the string may be in contact with the formation with a certain amount of the load carried by the suspending medium at the surface, and be stationary. Fourthly, the string may be in contact with the formation with a certain amount of load carried by the suspending medium at the surface, and be rotating.

In the first instance instability will occur only when a breakdown in the mechanical properties of the material occurs. In other words, if a stress within the elastic limit for the given material is applied, the resulting strain will disappear completely after the removal of the stress. If a stress beyond an elastic limit is applied, part of the resulting strain remains after the removal of the stress, and such a residual strain is called a permanent set.

In this first mode it is assumed that the only stress applied to the drill pipe is its own weight, since the string is freely suspended from the surface. It is very doubtful, therefore, in these circumstances, whether the limit can be reached for a considerable depth, since, with increasing depth, the weight of the drill pipe per foot is reduced. With a 10,000-foot well the size of the drill pipe would not exceed 3·5 inches, and this string would weigh approximately 60 tons. The cross-sectional area of the string is approximately 3·5 square inches, and the tensile strength of this pipe, assuming a safety factor of 2·5, is equivalent to 11,435 feet of pipe. This would give an

equivalent load to rupture the string, with no safety factor, of 380,200 lb. or 170 tons.

It will be seen, therefore, that with present-day standards, rupture of the string due to suspending it freely from the surface is a remote possibility.

To change the first mode to the second the string must be rotated, and here a condition of instability can arise due to this rotation.

It may be assumed that, at some depth well within the limits of modern holes, the drill pipe will tend to deform even when the bit is not in contact with the formation and is rotating. In other words, at some fixed depth, depending on the diameter of the drill pipe, the string will commence to deform spirally.

The spiral deformation would be of little consequence if it could be definite that the drill pipe is absolutely free from any eccentricity, but unfortunately this is seldom, if ever, the case, and the smallest eccentricity that exists will add considerably to the trouble occasioned by spiral deformation due to centrifugal forces.

Also great stresses are set up by torsional vibrations due to the long thin axis which is being used for drilling.

Capilushnikov [2] has determined mathematically the critical length of drill pipe at which deformation will take place even when the bit is not working on the formation. This critical length can be shown to be some function of the diameter of the drill pipe being used, its value depending on the value substituted for the intensity of shear stress. It has a value of 3842 D when f, the intensity of shear stress, is equal to 12,000 lb. per square inch.

The power is transmitted to the rotary bit by a vertical shaft the diameter of which is infinitely small compared with its length. The relationship between the diameter and length may ordinarily be between 1 and 10,000 and 1 and 40,000. Such an axis must of necessity be unstable, and any small external influence will result in the shaft leaving the vertical state.

With a ratio such as has been referred to, an analogy could be made to a length of sewing thread or the human hair. If a length of thread be held at one end and rotated, it will quickly be realized that the lower end of the thread will not rotate in a truly vertical plane, but will deform and rotate in a much larger circle. Or if this length of thread be held at one end and twisted at the other, the torsion will increase until a point is reached when the thread will become deformed into a loop or spiral. It may, of course, be difficult to imagine that a steel tube, say 4 inches in diameter and 6000 feet in length, could assume such a condition, but there is little doubt that the threads of the joints will be destroyed much more frequently by this means than by an excessive twisting moment in relation to the resistance of the material of the thread.

The value of the moment which determines whether the shaft shall retain its original straight form will, therefore, be necessary in any calculations pertaining to deformation of the drill pipe under torsion.

It can be shown, further, that a long thin axis can be spirally deformed when the twisting angle exceeds 450°. Thus, greater rigidity decreases the chances of deviation of the hole, and this has, of course, been realized for many years, and deviation has been overcome to some extent by the method previously referred to—namely, long, heavy drill collars.

For the third mode the string of drill pipe assumes the properties of a column. It is possible by means of Euler's Theory to determine the buckling length and buckling load for a given column, provided the column is very long in proportion to its cross section, is perfectly straight and homogeneous in quality, and the compressive loads are axially applied. These conditions cannot, of course, be obtained in practice, and the solution is best obtained by a consideration of the equations of equilibrium as formulated by Kirchhoff.

From these equations it is possible to determine the critical length at which the column will bend under a given load.

It is obvious that if the bit be allowed to rest on the formation before rotation of the drill pipe takes place, the unstable condition at the bottom will render the steering of the bit extremely difficult.

Finally, the fourth condition. In this mode the bit is in contact with the formation, a certain weight is allowed on the formation, and the bit is rotating.

From the foregoing it is possible for two states of instability to exist. First, that due to the long thin column resting on the formation with a certain load exerted on the column, and second that due to critical length.

An investigation of this mode will indicate that a third state of instability may occur due to the speed of rotation.

The relationship between bit pressure and cutting speed [3] was studied in one of the Oklahoma fields, and the results show that there is an almost constant increase in cutting speed, proportional to the increase in weight employed. It has been established that, when drilling with 6-inch drill pipe in sandstone requiring a pressure of 1000 lb. per inch of diameter, there will be insufficient weight on the bit for best results, even if the full weight of the string is imposed until a depth of at least 250 feet is reached. As the depth increases, the weight increases rapidly, until at 3000 feet only about one-eighth of the weight of the string should be permitted to bear on the bit and seven-eighths of the weight will be carried by the hook. The driller has therefore the difficult task of adjusting the feed to bring about a proper distribution of the load.

In addition to the critical moment, there is the speed at which the drill pipe is rotating, resulting in a state of whirl being set up. This question can be dealt with by considering the case of a loaded spring.[4]

If an elastic system such as a twisted shaft is disturbed from its position of equilibrium by the application of an additional force, of an external nature, the elastic forces of the shaft in the disturbed position will no longer be in equilibrium, and vibration will ensue.

In the general case an elastic system can perform vibrations of different modes, and a shaft, whilst vibrating, may assume the different shapes, depending on the number of modes subdividing the length of the member. A system having one degree of freedom is the simplest case, and the configuration of the system can be determined by one quantity only.

If a system such as the string of drill pipe, having several degrees of freedom, is examined, the result previously obtained for a system having one degree of freedom will be obtained.

It will be found, however, that for systems with two degrees of freedom two modes of vibration are possible, corresponding to two different roots of

the frequency equation, both of which are real positive roots. Each of these modes is called a normal mode of vibration.

In the general case of a system with "n" degrees of freedom it can be shown that the frequency equation is of the n^{th} degree, and that all the "n" roots of this equation are real and positive, provided vibration occurs about a position of stable equilibrium of the system.

An illustration of the general theory is a vertically stretched string with a number of equal and equidistant particles attached. From the equation of such a system it can be shown that the string may vibrate in the forms illustrated in Fig. 1. Type (*a*) represents the lowest or fundamental type

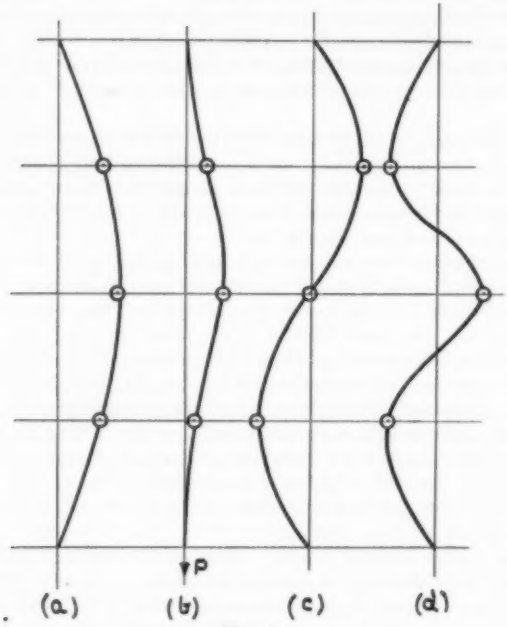


FIG. 1.

of vibration, its period being the largest. Type (*d*) is the highest type of vibration to which corresponds the highest frequency.

If an example is taken of 1500 feet of 6·625-inch diameter drill pipe, the lowest critical speed in air will be approximately 0·098 revolution per minute. Under these conditions, and realizing that the rotary table will be rotating at, say, 80 revolutions per minute, it appears that the shaft will be in a constant state of whirl.

Since the critical speed of 1500 feet of 6·625-inch drill pipe in air is 0·098 revolution per minute, it may be assumed that type (*c*) or (*d*) will exist in the well. In order that either of these types may be assumed to exist, an assumption must be made to the effect that the weight of the sections formed by the waves are concentrated at definite points throughout the string. If

such is the case, these weights will perform simple harmonic motions of the same period, $\frac{2\pi}{p}$, the period of natural vibration, and of the same phase α, passing simultaneously through their respective equilibrium positions.

From the example it appears that the shaft is in a constant state of whirl, and as the depth is increased this will become more serious. Obviously this cannot be true if the shaft is not to be ruptured continuously. It is quite possible that many twists-off have resulted from the effects of critical speeds.

In rotary drilling the hole is completely and continuously full of drilling fluid having a viscosity of perhaps 40 centipoises at 20° C., as compared with 0·018 centipoise at 20° C. for air. It would be expected that this viscosity would exert a viscous drag on the shaft which would have some effect on the critical speed.

Resisting forces which necessarily exist in such systems cause a gradual damping of the original vibrations. These damping forces may arise from several different sources, in this case from fluid friction.

When the damping is proportional to the velocity it can be shown that the period is

$$\tau = \frac{2\pi}{P_1} = \frac{2\pi}{\sqrt{p^2 - n^2}} \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where $n = \frac{\alpha g}{2W}$, in which W is the weight and α is a constant depending on the conditions.

If n is small in comparison with p, the difference between p_1 and p is a small quantity of the second order, and therefore it will be assumed that a small damping force proportional to the speed does not affect the period of vibration.

The amplitude of the vibrations gradually decreases with the time, and the vibrations originally generated will be gradually damped.

The rate of damping depends on the magnitude of the constant n.

The case of constant damping allows the following conclusions to be reached :—

A constant friction does not change the period of vibration.

Simply put, the critical speed is a function of the frequency, and damping will have no effect whatever on the frequency, but merely on the amplitude. This being so, a viscous liquid will not affect the critical speed, but will damp the whirl somewhat.

The annular space between the walls of the well and the drill pipe is not sufficiently great to permit the string to whirl seriously before the pipe is forced against the walls. This fact, coupled with that previously made that the whirl will be damped somewhat, will tend to prevent rupture of the string.

There is, of course, the possibility that the several factors which are intimately connected with the critical speed may be affected by the great depths being considered.

Experiments carried out on small-scale rods may not give comparable results, and in such circumstances the conclusions may not be correct. The calculation of the formulæ for critical speed makes the assumption that

the material from which the rod is made is homogeneous, but the formulæ are used under all conditions.

These factors, however, will not prevent the string from being in an unstable state. Motion of the drill pipe in the manner controlled by the foregoing conditions would result in the bit deviating from its true course, and nothing that the driller can do, other than reduce the speed of rotation of his drilling bit to such an amount that the fundamental type of vibration is reached, will prevent the bit from deviating. An increase in pump pressure will assist in maintaining tension in the pipe, and may be of some assistance.

It has been mentioned that at a given depth the drill pipe will deform spirally as a result of its length, irrespective of whether the bit is operating or not. At this critical depth, therefore, the bit will progress in any direction, depending on a number of factors. The lower end of the drill stem is in a definitely unstable condition, and the possibility of deviation of the hole is thus considerably increased. Critical depth may, therefore, be considered an important factor in holes leaving the truly vertical path after a given depth has been reached. No external forces, such as changing formations, extraneous material in the hole or any other factor which might result in the bit being turned away from its true course, need be present to cause the bit to deviate.

From data obtained from rotary-drilled holes it has become apparent that there exists another condition resulting in the bit deviating from its true course. These data show that in general the deviation measurements increase with depth, and the obvious conclusion to be reached is that the hole assumes a gentle curve, and does not take the form of a spiral or any other form of curve which would necessitate the course of the hole fluctuating from up-dip to down-dip and back again.

Deviation of rotary-drilled holes is in general in the up-dip direction, and this has been shown clearly in cases where a deviated hole has been straightened. Numerous cases have been noted where the hole has remained normal to the bedding planes, and in all cases of this sort the direction of deviation is up-dip.

Leaving aside the instability of a drilling string due to critical depth, it is obvious that, when a bore-hole deviates, there must exist extraneous forces acting on the string. At present there are no means of determining the nature of these forces, and the only thing possible is to split them up into one vertical component, one horizontal component parallel to the strike and one horizontal component parallel to the dip. In an up-dip tendency the horizontal component at right angles to the strike has the greater influence in that direction. Where the bedding planes are lying horizontally there will be no lateral forces acting, and therefore no tendency to deviate.

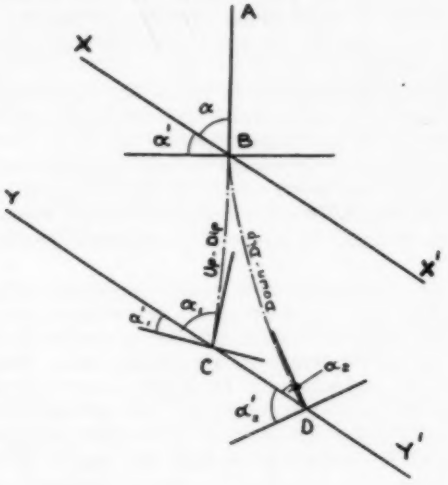
With regard to an up-dip deviation, it should be noted that no deviation from the vertical greater than the angle of dip of the bedding planes with respect to the horizontal is possible.

Under conditions in which the critical angle is not reached, therefore, the tendency of a rotary drilled hole will be in an up-dip direction, or, in other words, the bit will endeavour at all times to drill normal to the bedding planes.

Let the bedding planes lie at a steeper angle than was assumed in the normal case.

In Fig. 2 let AB represent a truly vertical hole striking a bedding plane and making an angle α with it, and assume that the hole will have no particular tendency to deviate either up- or down-dip. Angle α may then be called the critical angle.

Let now an external force act upon the bit to cause it to deviate to point C, so that α_1, is less than α. The bit will then continue to drill up-dip. If instead of diverting the bit to C the external force has caused it to travel to D, so that α_2 is greater than α, the bit will continue to travel down-dip.



CRITICAL ANGLE

FIG. 2.

It is obvious from the foregoing that conditions as indicated by AB are very unstable, and factors outside the driller's control may cause the hole to deviate in either direction.

The case may quite easily arise of formations dipping in opposite directions on either side of a fault. In such a case the bit may travel in an up-dip direction until the fault is reached, and then in a down-dip direction after passing the fault.

Although it is generally agreed that a critical angle of dip does exist, the value of this angle has not been determined. Its existence will depend on a number of variables the values of which are difficult of assessment. This angle will vary with the relative hardness of the strata, with the characteristics of the bit and with the angle of the dip.

It may be written.

Critical angle $\propto$ ø (bit), ø (dip angle), ø $\left(\frac{\text{hardness}_1}{\text{hardness}_2}\right)$.

For the purposes of an examination of the effects on drilling, the actual value is of no importance, and a simple illustration will suffice. Assume that the bit is drilling in a soft formation and is about to enter a harder one. If the string is assumed to be perfectly straight and the formations to be lying horizontally, there will be no necessity for the bit to travel in any other direction than vertically.

Assume now that the formations are turned through an angle. As the angle increases a point will be reached when the bit can no longer cut into the hard formation, and the path of least resistance is down the interface between the soft and the hard strata. Sliding will therefore take place.

The angle at which the bit will travel up or down the dip is that referred to as the Critical Angle.

From this simple illustration it is fairly obvious that no definite number of degrees can be given to the Critical Angle which will differ with different kinds of grounds and with different types of bits.

Bruges [5] endeavoured to determine the critical angle, and, although it is no doubt difficult to express in a formula factors dependent on so many and obscure variables, the result obtained definitely shows that a critical angle does exist, and that in the conditions assumed will have the value found.

From these calculations and from results obtained by using the Martiensen Surveying Apparatus to check up the deviations of a number of wells, Bruges states that when the critical angle is exceeded the bit will slide down-dip and bite against the down-dip side of the hole. Where the critical angle is not reached and where the bit leaves a soft formation to enter a harder one, the hole will change direction and proceed up-dip. In other words, the bit will endeavour at all times to drill at right angles to the formation until such an angle is reached that this is no longer possible, and the bit will then take the direction of least resistance and travel down the interface between the soft and the hard formations.

Once again the actual value of the critical angle does not matter. It is sufficient to say that an angle does exist, and this being the case, the direction of the bit is problematical, even though the necessary precautions may be taken.

Instances arise where tools are unavoidably left in drill holes, and it is found impossible to remove them and yet it is necessary to continue the hole. Such a case would arise when great depths have been reached and large amounts of casing have been landed and cemented. In order to prevent wastage of money by abandoning the well, efforts are made to side-track the lost tools.

In this operation a whipstock is used. This tool is made of forged steel or cast iron, and thickens towards the lower end, giving a slanting face down which the drilling tool can slide. The whipstock is lowered to the top of the lost tools, and may be cemented in place.

The bit is then made to work down this slanting face, and so be diverted past the lost tools. If the hole in which the lost tools were working were perfectly vertical, it is obvious that the new hole formed by the bit sliding down the whipstock would be deviated. If the first hole were crooked, there is the possibility that the hole may be straightened. On the other hand, the probability of further deviation must not be overlooked.

In the rotary system, then, drilling is done by a long thin axis which can be shown to be completely unstable at some critical depth, Kd, where K has some value such as 3842 and d is the diameter. At this critical depth the driller can have little or no control over the direction in which the bit will progress. In addition, a sudden change of formation, as from a soft formation to a hard one, where the strata are lying at an angle greater than the critical angle or where the strata are lying at an angle less than the critical angle but the string is bent due to the application of incorrect weight, or if the critical length has been passed with any amount of weight on the bit, will result in the bit deviating from the vertical path, and nothing that the driller can do will prevent this.

Drill pipe is seldom, if ever, mathematically straight, and the eccentricities in the pipe will add to the ease with which the stem deviates, and critical length and sudden change of formation merely multiply the troubles.

Even Hayward's hypothesis does not assist in overcoming this tendency to deviate if the critical length theory is accepted.

These main points show clearly that drilling by the rotary system is impossible of complete control, and completely vertical holes are the exception rather than the rule.

PART II.

Deviated Drilling.

In January 1934 a method of drilling known as Controlled or Directional Drilling was brought prominently to the notice of operators by the drilling of a deviated relief well at Conroe to enable a neighbouring well, which had got out of control, to be killed.

By means of this system of drilling, operators are able to complete their wells at any approximate point reasonably distant from the vertical. In many of the Gulf Coast districts it has become an accepted practice, and particularly in fields where a short horizontal drift may represent the difference between success and failure.

Directed or controlled drilling, as the name is intended to convey, means the controlled steering of the drill stem in the desired direction to a given location below the surface.

This practice has not been used altogether to establish and maintain a definite drift or deviation, but has been used to straighten holes, side-track lost equipment and to obtain geological information by drilling a number of shallow wells from the same location. Although directional drilling is usually looked upon as a method for drilling away from the vertical, the same principles apply for bringing a well which has deviated back to the vertical.

In this latter statement it is seen that the theory applicable to straight-hole drilling technique must apply to deviated drilling technique. It will be shown later that the problems which make straight-hole drilling difficult also make directed drilling difficult.

Drill holes may take one of four forms: (1) vertical; (2) inclined; (3) curved; (4) crooked.

The crooked hole may quite easily result from straightening efforts which cause a dogleg hole.

In directional drilling (2) and (3) are the forms aimed at.

On one flank of the Barber's Hill field the natural tendency is to drift down-structure and to produce only water. Several wells, it is recorded,[6] have recently been drifted up-structure with good results. By directing the course of the wells towards the salt plug, portions of the producing zone, yielding clean oil, were opened.

An instance of directing the bit out of the salt plug is recorded from the same field. In this case the salt was struck at 1100 feet, and although drilling was continued to 5600 feet, it was impossible to get out of it. The hole was therefore plugged back to 4000 feet, and the direction of the hole changed by directional methods.

In the Hackberry field a well showed a tendency to wander in the wrong direction, due to structural conditions and bit action, and it required the use of four whipstocks before the well could be swung into the proper direction.

In the Huntingdon Beach field [7] a large number of wells were drilled by controlled directional methods, with a view to extending the productive area of that field by tapping oil reserves beneath the ocean in the vicinity of the field. The maximum drift angle resulting from controlled directional drilling was as much as 78 degrees.

The inclination of a hole permits of a much larger sand penetration than would be possible with a vertical hole, irrespective of whether the oil formation lies at an angle or is horizontal. This will naturally affect the present productivity, and in certain circumstances the ultimate productivity of the well.

Directed drilling enables the sand to be tapped in inaccessible places such as occurred in the Signal Hill field. In this instance the productive zone underlying the Sunnyside Cemetery was entered from a location situated away from the cemetery itself.

Inaccessible locations such as submerged or precipitous ones can be avoided by directed drilling, and a considerable depth of hole may be saved by selecting a suitable site.

Off-shore locations can be drilled and a considerable saving in erection costs shown by drilling a number of holes from the same foundation and derrick. By properly directing the bit, six or seven normal locations can be penetrated.

Directed drilling may be accomplished with or without the use of deflecting tools. The conditions of the hole and the character of the formations to be penetrated, and particularly the experience of the operator, are of vital importance.

As an instance of directed drilling without the aid of deflecting tools, the recent experiment of the Barnsdall Oil Company of California [8] may be quoted. This Company drilled three wells from one location, and although this experiment is not strictly one of directed drilling, but a modification of it, it has shown that a great saving can be effected where a number of wells are drilled in this manner.

Another instance in which directed drilling proved itself to be of value was in the case of the Alexander No. 1 well, which had broken away

and cratered. In drilling an emergency relief well to enable the flow in the cratered well to be shut off, the feasibility of directed drilling where deviation from the vertical and direction of drift must be exact has been demonstrated. It was decided to drill a relief well and aim at hitting the producing sand as near as possible to the bottom of the cratered well. It should be mentioned that the actual course of the cratered well was practically unknown, since only below 3500 feet had it been surveyed, and then only by acid bottle. It was assumed, however, that, since the acid bottle readings showed the well to be reasonably straight, the hole was straight. Such an assumption was probably unjustified, and the final landing point of the relief well might have been far removed from the bottom of the cratered well.

The relief well location was 412 feet from the cratered well, and only a gentle drift was necessary to reach the objective at about 5100 feet.

A vertical hole was drilled to about 1400 feet, and a string of 13⅜-inch casing was cemented at 1414 feet. The hole was then continued in the ordinary way until 1960 feet had been drilled. At this point a careful survey was made and plans for deflecting the hole were completed.

At 1960 feet a patented universal-joint deflecting tool was run and 20 feet of hole were made. This tool was then pulled from the hole and a survey carried out. The desired drift having been obtained, the hole was continued with the regular drilling tools.

At the end of each 100 feet a survey was carried out, and any deviations from the desired course were adjusted by controlling the weight, speed of control and by carefully selecting the drilling bits.

Single shot surveys were made, and as a check oriented drill-pipe tests were carried out.

At 5135 feet drilling was stopped, and the bottom of the relief well was calculated to be a very short distance from a vertical line drawn from the top of the cratered well. The relief well drifted 292 feet south and 291 feet west with a total drift of 411 feet.

The formations in the Conroe field are ideal for directional drilling, as they lie practically flat and there is an absence of faults.

A large number of tools, to assist in controlling the drift and to enable the necessary deflection to be obtained, are available.

In easily drilled formations a knuckle joint is utilized. This has a universal joint incorporated immediately below the tool joint. Attached to the universal joint and hanging down at a fixed angle is what is called the "stinger," which is fitted with a diamond point four-way bit at the lower end. In order that the small hole made by the diamond point bit may be enlarged, a reamer is built into the "stinger" near the upper end. Immediately above the reamer a stiff spring is placed to stiffen the action of the universal joint while the tools are being lowered into the hole.

The tool is oriented into the hole in order that the direction that the angle of the knuckle joint will take may be controlled. The tool is dropped into the formation when the direction of the "stinger" has been calculated.

It is claimed by the makers of this tool that, provided the speed of rotation and the weight are correct, complete control of direction is possible.

When the desired angle of deflection has been obtained, the knuckle joint is removed and an ordinary fishtail bit is run in, provided the formation

does not change perceptibly or the hole appears not to be running out of hand.

If instead of a soft formation at the commencement there is, say, limestone, a removable whipstock is used to begin the deflection of the hole. This tool may be of heavy forged steel or tough cast iron, but in either case the shape is the same. The upper end is equipped with a collar, and the body gradually thickens toward the point, which terminates in a wedge so that it may be stabbed into the formation to prevent rotation.

The whipstock is attached to the drill pipe by inserting the tool joint on the lower end through it, so that a pin may be driven through a corresponding hole in the collar of the whipstock into the hole in the bit.

Rotation of the whipstock is thus prevented. The tool is oriented into the hole in exactly the same manner as for the knuckle joint, and when the bottom of the hole is reached the whipstock is secured to the formation by setting the spade point sharply into the wall of the hole, and this operation breaks the pin securing it to the special bit. The whipstock is forged with a channel on the inner side, so that the bit will be forced to follow the proper course, and so assume the correct angle of deviation.

Drilling is performed in the usual manner, with the speed of rotation and the weight on the bit properly controlled. When about a length of drill pipe has been lowered, the tools are removed from the hole, and since the special bit has a body larger than the collar of the whipstock, it removes this tool from the hole as the drill pipe is removed. The hole has thus been started in the correct direction, and a bit of the size required will continue the hole.

Another type of tool, known as a hydraulicking spudding bit, may be used in very soft and unconsolidating formations. This bit is oriented into the hole and faced in the desired direction. Weight is applied and the pumps are started. The jetting action of the fluid from the nozzle, combined with the spudding, allows the bit to slide off at an angle. A few feet only will be made with this bit. The string is then run with a length of small-sized pipe at the lower end to give additional flexibility.

Surveys are made to insure that the direction of the hole has been properly changed. Any type of surveying instrument which will give deviation and orientation can be used.

Two methods of orienting the drill pipe into the hole are available, both using the same principle.

It is interesting to note that disagreement as to the accuracy of surveys based on the practice of orienting drill pipe exists among engineers. Many claim that the pipe is twisted on lowering it into a crooked hole, where there is considerable friction, with the result that there is no relation between the direction of a radial plane through a certain point on its circumference at a depth of several thousand feet and the direction that this plane assumed at the surface.

An error in orientation will definitely result in the hole deviating in an incorrect direction, and detection is possible only by running a surveying instrument capable of recording both deviation and orientation.

It has been found that different types of bits have definite tendencies in deflecting. For example, the drag-type bit will generally go to the right and the wheel-type bit will tend to go to the left. Where rock bits are

used, the tendency is for the wells to turn to the left. With these tendencies it should be possible to deflect a hole in various directions merely by the use of different bits. Unfortunately, nothing definite can be stated regarding the direction in which these bits will deviate, and the point of the compass to which the bits will travel is impossible of determination. The bit can turn to the left or right throughout the 360 degrees, and steering is possible for deviation only.

One writer, when dealing with the subject of directed drilling, observed that several wells had met under ground, but thought it was remarkable how well the casing ran into most holes except where bad kinks had formed due to the hard formation not being suitable for directed drilling.

By that statement the technique of directed drilling aligns itself with that of straight-hole drilling, and the difficulties of the one will be found in the other.

Experience would appear to be the greater guarantee of success in directing a bit to a desired location, and a knowledge of the position of the hole at all times is an absolute necessity of successful directed drilling.

Apart from the use of deflected tools, it will be found that the deflecting of a bit to a desired position becomes as difficult as the steering of the bit in a vertical path.

PART III.

Discussion of Straight-Hole and Directed-Hole Drilling Technique.

In Part I a theoretical examination of straight-hole drilling was undertaken and the various factors affecting such practice were examined.

In order to assist the examination of directed drilling technique as it is affected by these factors, they will be listed:

(1) It was shown that, with the possible exception of the rotary table and the slush pumps, improvements in the surface equipment could have no effect on the direction of the hole;
(2) An alteration in the type of bit being used might possibly assist in the maintenance of a straight hole;
(3) Only a reasonable weight should be permitted on the bit;
(4) Bit must be maintained true to gauge;
(5) Correct pump pressure should be maintained;
(6) Drill pipe must be kept in tension;
(7) Uniform rate of feed to be applied;
(8) Critical speed of drill-pipe resulting in a high type of vibration;
(9) Critical depth;
(10) Critical angle of formations.

In Part II a description of a new method of drilling so far as the oil industry is concerned, known as Directed or Controlled Drilling, was given. The manner in which this system is carried out and the occasions on which it would be used were also explained. This method, as was seen, consists in the deliberate drifting of bore-holes, and the arguments put forward would appear to be a complete contradiction of those advanced in Part I.

Part III will, therefore, be devoted to an examination of those arguments in the light of the various factors which were shown to be detrimental to the drilling of straight holes.

In straight-hole drilling it was seen that the surface equipment, with the possible exception of the rotary table and the slush pumps, could be of no assistance whatever in the drilling of a vertical hole. The hydraulic table assisted somewhat by permitting the use of flush-jointed drill pipe larger than was possible with the ordinary rotary table. The pumps could be used to place a tension in the lower portions of the drilling string, and so maintain the string in the vertical state while additional loads were added.

With directed drilling the object is to steer the bit to a position not immediately below the starting point on the surface. Neither the hydraulic rotary nor the slush pumps can be of any assistance, since both these portions of the surface equipment tend to maintain the string in a vertical state.

When the diameter of the drilling string is increased, the operation of flexing becomes more difficult; that, as was seen, is the object of increasing the size of the diameter. Hayward's hypothesis cannot assist in directing the bit in any other direction than the vertical, since only when an excess of tension is applied to the drilling string is any benefit obtained. Any degree of pressure below that absolutely necessary to maintain the string in an extended state will have no effect on the drilling string beyond a certain depth. If the pressure is reduced to a figure just sufficient to maintain flow of mud fluid, the string will be influenced little or not at all, and directing the bit to a desired position could be accomplished just as easily without any fluid flow. There is the possibility that the addition of pressure to the string after the bit has commenced to drift will enable the direction of the bit to be changed, but such an operation must of necessity be difficult, since several factors will oppose any change of direction.

An alteration in the type of bit being used would be of assistance if definite data were available on the directions in which each type of bit tends to deviate. Nothing definite can be laid down with regard to bits, and since this is so, the possibility of a drag bit moving to the left when it has been used to cause a deflection to the right must not be overlooked. A similar result may be experienced when using rock bits and disc bits.

It is reported that holes have been deviated in certain fields in America by using different types of bits in the different types of formations, and without the use of deflecting tools. It is explained that this is possible only because of the fact that the formations are thoroughly understood. It might be assumed that the formations are ideal for directional drilling, and that the fields are free from faults, since a knowledge of the formations cannot help in any way to keep the bit on its directed course.

The amount of weight on the bit can assist directional drilling only by flexing the string, and the exact amount of flexing which a given weight will cause cannot possibly be estimated. No two strings of drill pipe have the same degree of straightness, and therefore the same added weight will have a different effect on different strings. The wall thickness of the drill pipe varies slightly throughout its length, and hence will be weaker in some sections than in others. It will therefore flex much more easily in some places than in others, and give a different degree of deviation. The

formation in which the bit is working will also affect the degree of flexing, since, in a soft formation, additional weight may only cause the bit to dig faster, whilst in a hard formation the pipe will definitely flex. Between maximum and minimum hardness there will be maximum and minimum flexing for the addition of a given load.

The maintenance of the correct gauge for the bit is a vital factor in all drilling, not only in keeping a correct size hole, but also in keeping the bit on a vertical course. It is as necessary to keep the bit true to gauge when drilling a directed hole as it is when drilling a straight hole. If the bit will wander from the vertical path due to the gauge becoming incorrect when drilling vertically, exactly the same thing will happen when drilling by the directed methods. In this case the bit will wander away from the path desired without the driller having any control over it.

The question of pump pressure has been dealt with earlier.

Maintaining the string in tension would result in the drilling of a straight hole and, provided deflecting tools are used, a deviated hole could be possible under the same conditions. If no deflecting tool is used, it would be necessary to remove a certain amount of tension from the string in order to permit the string to flex.

It was seen that, when drilling a vertical hole, it was necessary to maintain a uniform rate of feed, as deviated holes result from the intermittent use of the brake during drilling, especially when the bit is dropped into a soft formation. Obviously a deviated hole could not possibly be started by the use of such a problematical method, and this factor of straight-hole drilling can therefore be of no assistance in directional drilling. Further, in directed drilling it will be equally necessary to maintain the same uniformity of feed.

It was shown that, at the normal speeds of rotation for rotary drills, the critical speed exists as soon as the table commences to rotate. As a result of this critical speed, the drill pipe assumes a configuration of a type showing the highest frequency. Consequently, the string is composed of a series of waves and a critical speed exists throughout each wave. With directional drilling, precisely the same conditions exist, unless the speed of rotation is reduced to such a figure that the configuration of the string represents the lowest or fundamental type of vibration. At this speed progress will be very slow and drilling almost impossible. Because of the configuration assumed by the drilling string, the directing of the bit becomes a difficult matter.

By far the most important factor opposing the drilling of straight holes is the critical depth. It was stated that there is a definite depth at which the string becomes unstable at its lower end. This was at some such depth as Kd. In the conditions assumed K is equal to 3842.

This critical depth is unaffected by anything, even by the use of deflecting tools, and therefore applies to directional drilling just as much as it does to straight-hole drilling.

What is the effect of the critical depth on directional drilling? When the bit arrives at a depth corresponding to some such factor as Kd, where K in this case is equal to 3842, the bit begins to wander, irrespective of the precautions taken by the driller. The moment that an external force such as a hard stratum, a boulder, etc., acts on the lower portion of the

string, the driller loses control of the bit. The fact that the bit is being directed can have no effect on this phenomenon. It is clear, therefore, that the directing of a bit is no longer possible once the critical depth has been passed and the string is subject to factors beyond the operator's control.

The final factor is that of critical angle, and it is clear that exactly the same condition will exist for both straight-hole and deviated drilling. Examining the condition which may arise due to this critical angle, it will be seen that the possibilities of steering the bit to a desired point become more remote and the necessity for a constant check on the hole more important.

It has been shown that the bit will always endeavour to drill at right angles to the formation until such an angle is reached that this is no longer possible, and that the bit would then take the direction of least resistance and travel down the interface between the soft and the hard formation.

If that statement is true—and there seems little reason to doubt it, although the exact angle at which the bit will travel down the interface cannot be determined, and is probably a variable dependent on formation hardness—it is possible to see the effect on directional drilling by assuming that the formations are lying horizontally. This would be the simplest case.

The bit is driven downward vertically for a short distance, and, provided the weight on the bit, the speed of rotation of the string and the mud pressure exerted on the lower end of the string are correct, the bit will tend to follow a relatively straight path until the critical depth is reached. If, now, prior to reaching the critical depth the string is diverted by one of the available means, either knuckle joint or whipstock, an angle may be reached such that sliding takes place. In other words, the critical angle will be exceeded, and the bit can no longer bite into the formations when encountering a harder formation, and will follow the direction of the interface between the formations. If the angle at which the string is deviated is less than the critical angle, the bit will continue along the deviated path, provided no other factors are allowed to affect it.

If instead of drilling in perfectly horizontal strata the bit is working in strata inclined as shown in Fig. 3, and the point to be reach is A'.

Let the tangent to the direction in which the bit is progressing make an angle α with the planes, and let this angle be such that the bit will continue to progress in the deviated direction. By the hypothesis of the critical angle, if during drilling this angle is reached the unstable condition will arise, and the driller will have no control over the direction in which the bit will progress. In the example given the bit would have turned down the plane between the interface, and would have arrived at a spot some distance above the spot desired.

Precisely the same argument could have been put forward for a formation inclined in the opposite direction, or, for that matter, in any direction around the circle.

The desire to increase oil-sand penetration by slanting the hole in a down-dip direction requires no special technique, and the use of such an instrument as a single-shot survey instrument, giving both inclination and the direction of the open hole, is all that is necessary to ensure that the bit is

progressing away from the vertical. No actual position is aimed at, and provided an increase in penetration is obtained, the actual path of the bit is of little account. This is one application of the directed drilling practice.

The drilling of wells from favourable locations is one of the important uses for directed drilling. The selection of a site to overcome inaccessibility may require that the bit should travel across a fault plane in order to reach the desired oil sand. Such an instance is shown in Fig. 4. This figure illustrates the use of directed drilling to overcome conditions of inaccessibility, together with the necessity of crossing a fault plane. AA' is the fault plane, and AB is the ground surface on which the wells are started in preference to AC.

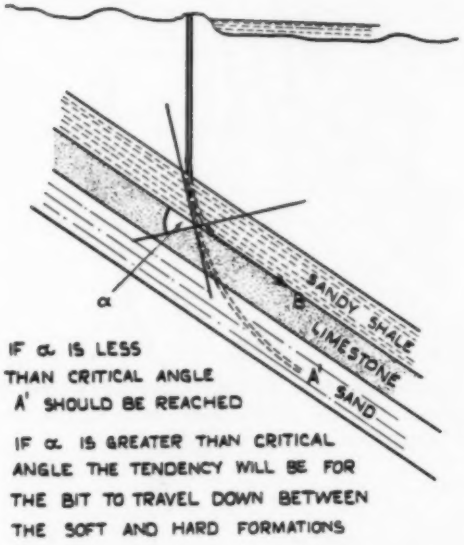


FIG. 3.

In the four cases shown, if the formation on the right of the fault be assumed to be softer than that immediately opposite on the left-hand side of the fault, and the angle at which the fault plane is tilted is such that the critical angle is exceeded, the bit will follow down the plane, and not across it, with the result that the bit will not be directed to the desired sand.

If the strata on the right-hand side of the fault plane be assumed hard and inclined downwards from the plane, as shown by the dotted section M, and the angle is such that the critical angle is also reached, the bit will follow down the interface between a soft and a hard formation, since that is the line of least resistance.

If, on the other hand, the strata tilts in the direction shown by section N, so that the critical angle is reached in that direction, the bit will move down the interface, and will penetrate formations on the left-hand side of the fault

plane. Whether the oil sand will be penetrated will depend entirely on the position of the hard stratum compared with the oil stratum.

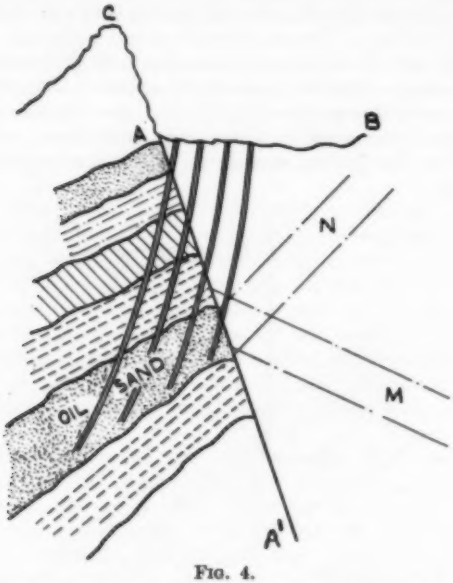


FIG. 4.

If now the fault plane lies at such a shallow angle that the directed bit attempts to cross it with the critical angle reached, the bit will travel up the fault plane away from its objective (Fig. 5).

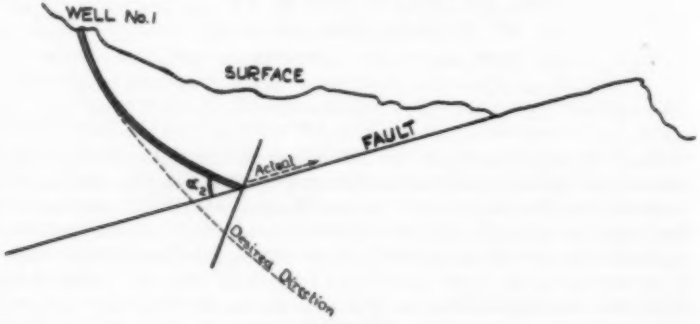


FIG. 5.

Another example of directed drilling may be taken from the Long Beach field. In this case a condition existed where, if the well were drilled vertically, it would be unproductive, and it was necessary to direct the well up-structure to obtain production. This is shown in Fig. 6.

Well No. 1 would have been unproductive if it had been drilled vertically, but by directed drilling the well became productive. This is an instance in which surveying the hole regularly would be all that was necessary, and no special rules would be required. Well No. 2, on the other hand, has to pass a fault plane, and, as in the previous illustration, the path of the bit will depend entirely on the angle at which the fault plane is lying with respect to the hole. As shown in Fig. 4, the critical angle will undoubtedly be reached, and the bit may travel down the fault plane and entirely miss the productive zone.

Assume now that the hole passes through a hard formation prior to meeting the fault plane. The tendency in such a case will be to force the

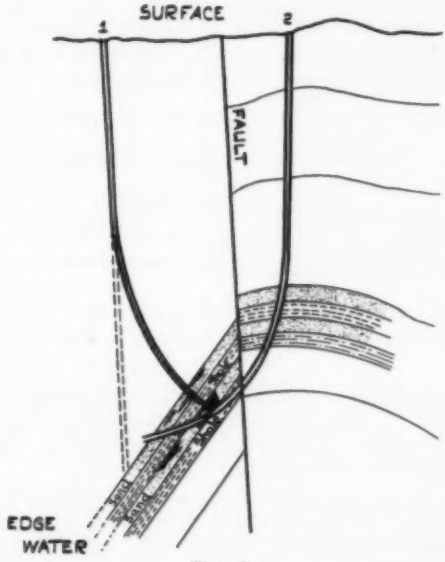


FIG. 6.

bit more into the vertical. This results from the shoulder formed by the hard formation at the fault plane. The angle from the true path which the bit will be forced to take will be small, but over great depths the discrepancy in the position reached by the bit may be great. Only by enlarging the hole in the hard stratum, by means of a reamer or other appropriate tool, to do away with the shoulder, is it possible to be certain that the bit will enter the sand at the desired angle (Fig. 7).

Considering the factor of critical depth, it will be seen that its effect is to increase the difficulty of landing the bit in the desired position.

The instability of the lower end of the string, when the critical length has been reached, is such that any extraneous force will cause the bit to move along any path of least resistance. In such circumstances difference in hardness between the sides of the fault-plane may not be necessary.

The zone of weakness between the up-throw side and the down-throw side would be sufficient to cause instability and to encourage the string to follow down the fault plane.

In Fig. 6 also the string is shown as having turned upward into the oil sand. Once again it is clear that if the oil reservoir is a limestone, the bit will tend to travel down the interface between the limestone and the shale, and the oil zone would have been missed.

It is possible to conceive a case when the bit turns in the soft formation, due to the instability which arises from the critical length factor, before the hard formation is reached, and its direction may be anywhere. Since the instability does arise, the bit may then turn again to work against the hard formation at an angle which will prevent sliding. The bit will then commence to work in the hard formation until such time as the instability can once again take affect to turn the bit in another direction.

The direction the bit will take, in such circumstances, will be completely out of the driller's control, and the use of deflecting tools for directing it

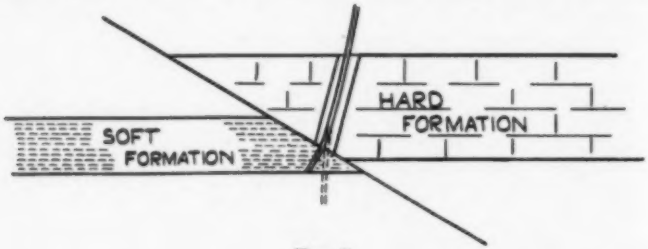


FIG. 7.

will be of little value unless such tools can be used throughout the complete length of the hole. If a depth is permitted between the placing of the tools such that instability can take effect, the direction the bit takes will be completely outside the driller's control.

Mention has been made of the tendencies of different types of bits to deviate on their own account and the difficulty of using directed drilling methods in certain formations on account of the failure of the bits to drill a smooth hole. Unfortunately, when attempting to direct a bit in certain hard formations, the bit forms a series of steps in which casing and tubing can catch up. The formation of these steps increases the difficulties encountered in holding the well to its objective, and excludes areas in which these hard formations are found from the satisfactory use of directed drilling.

Without the use of tools for directing the bit, it is apparent that the driller cannot possibly be certain that the bit will reach the desired position, except in such circumstances that all the affecting factors are towards that position, and no amount of care in placing definite loads on the bit or in adjusting the mud pressure or the speed of rotation of the bit will have any effect whatever.

The effects of critical depth and critical angle are definitely cumulative, and, thus, if the two factors are in opposition, there is always the possibility of the bit reaching the point desired. This would result if, for instance,

the bit turned in one direction due to instability resulting from the critical depth, and the formation was at such an angle that the bit was forced into the desired direction.

Referring again to the one instance recorded where a definite point was aimed at.

It is impossible to be certain that the bottom of the relief well was near the bottom of the cratered well, since no data were available on the condition of the cratered well, except for the acid bottle readings of the last 1600 feet. All that can be known is that the relief well was deviated to the sand from which the cratered well was producing, and that the direction was correct. Water pumped through the relief well into the sand at the proper pressure would be forced to move from a high-pressure to a low-pressure area, and that would be towards the producing well, where the pressure is atmospheric at the mouth.

Distance from the bottom of the relief well would not, within reasonable limits, be of very great moment, since the operators would be unable to determine with any accuracy the amount of pressure needed to force the water from the relief well into the cratered well to kill it.

The fact that the relief well arrived at or near the spot desired does not in any way break down the theory proposed by the critical length and critical angle hypothesis, since the depth drilled definitely exceeded the critical length. Neither would the speed of rotation, control of weight and selection of bits have any bearing whatever on the direction after the critical length had been passed.

This being so, it is safe to say that the successful drilling of the relief well was achieved in spite of opposing factors and because of the favourable formations of the Conroe field.

The drilling of most deviated wells takes little or no account of the actual position at which the bit will arrive and the incorrect drilling of a vertical well would suffice. In other words, if multiple drilling is to be tried, it is immaterial where the holes reach, provided all the holes are bottomed in the producing zone.

The statement that several holes met underground, may be taken as evidence that directed drilling is not the success claimed for it after the drilling of the Conroe relief well.

It may be claimed from the foregoing that what success may have been achieved in deviated-drilling projects can only have resulted despite opposing factors and from persistent surveying throughout the hole. Without such surveying the chances of success would be remote, if not impossible, and the cost of drilling the directed hole must of necessity be considerably greater than for a vertical hole. By the constant use of instruments it is possible to steer the bit at a definite angle until the critical depth is reached, but there is always the possibility of the bit turning in a direction other than that desired.

Where the directed hole is started in order to obtain a more favourable site, it is questionable whether the increase in time and money will be compensatory.

Where, due to foundation difficulties, it is desired to drill a number of holes from the same foundation, deviated drilling would be entirely satisfactory, since the exact position the hole is to strike is not altogether im-

portant, and it has been shown that such drilling is not only possible, but has been practised for many years under the guise of straight-hole drilling.

The possibility of turning the bit away from a surface site to a position under another's land giving increased production would naturally be made use of by operators whose lands are either barren or giving small production. It is difficult to discover where this is being practised, but a case has recently been before the American Courts, and the result is awaited with some interest.

The title "Controlled or Directed Drilling" would appear to be a misnomer from the evidence put forward, and a more correct title would be "Deviated Drilling." This title would cover all cases, whether the well is bottomed at a particular point or, as is more likely, merely deviated from the vertical path in order to penetrate a producing zone in some position immediately below an inaccessible surface position.

From the evidence put forward it is clear that none of the factors required for straight-hole drilling can be of value in directed drilling. Only by the constant use of deflecting tools and regular surveying will it be possible to control the direction of the bit in directed drilling, and then only up to the critical depth. After that point is reached nothing can possibly be done to control the bit. A complete knowledge of the formations will enable whipstocks to be set for the crossing of fault planes, or the interfaces between soft and hard formations lying at angles greater than the critical angle. Without the use of such deflecting tools the bit will travel as the critical angle demands.

It will be recognized that directed drilling is more complicated than straight-hole drilling and success far less certain.

Conclusions.

1. Straight-hole and directed-drilling technique are exactly the same when deflecting tools are not used for the latter type. It is immaterial whether the bit is to be steered to a point vertically below the starting point or to a point some distance removed. Exactly the same difficulties arise with regard to the actual steering, but, if external forces are acting on the bit, there is always the possibility that they will be in favour of the bit and not opposed to it.

2. In straight-hole drilling up to the critical depth, and excluding any action of the critical angle, control of the weight on the bit, of the pump pressure and the speed of rotation will definitely produce a vertical hole. The action of the critical angle of the formations will oppose the effects of these factors, and may result in the drilling of a crooked hole.

3. In directed drilling the control of weight, mud pressure and speed of rotation in order to cause deflection become so difficult that their effects can only be problematical. The steering of a bit by means of such factors is possible, but the exact amount of flexing or the direction in which the bit will travel cannot possibly be determined.

4. After the critical depth has been passed nothing that the driller can do will make the steering of the bit more definite. The instability of the string is such that the bit may travel in any direction in suitable formations, and neither whipstocks nor any other type of deflecting tool can have any

effect except for the small region actually surrounding the tool. Once this region is passed the critical depth factor will once again operate.

5. The critical angle hypothesis has been accepted for a long period, and, as has been seen, is dependent on the characteristics of the bit used, the angle from the horizontal at which the dip is lying, and on the relative hardness of the formation drilled through.

With a complete knowledge of these three variables, it is possible that the effect of critical angle can be overcome.

6. Nothing appears possible to prevent the long, thin circular shaft from deflecting when the speed of rotation reaches the critical speed. At this speed instability sets in, and, depending on the mode of vibration, so the string will assume a definite form. The centre line of the shaft will never coincide with mathematical exactness with the axis of rotation owing to want of straightness, vibration, incorrect weight on the bit and other causes, and, as a result, centrifugal forces due to the inertia of the shaft will produce deflection, increased deflection resulting in increased centrifugal forces.

An endeavour has been made to examine the technique of drilling theoretically, and the details of procedure which are trade secrets have not been considered. It is possible, of course, that many of the arguments put forward will be contested by experienced drillers, but the fact remains that drilling by the rotary method makes the steering of the bit to a particular position a particularly difficult problem. With increasing depth, and consequent decreasing size of diameter of drill pipe, this problem is being accentuated.

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FACTORS AFFECTING THE DESIGN OF BUBBLE-CAP COLUMNS.*

By L. C. Strang, B.Sc., Ph.D.

Among the factors affecting the design of fractionating columns, particular attention must be paid to the economic considerations which call for a column that has the highest capacity for its size and cost. For this reason the design of bubble-caps to produce intimate contact between liquid and vapour with minimum entrainment of liquid particles by the rising vapour is of practical importance.

The greatest permissible vapour velocity is limited by two considerations, viz. :—

(*a*) Entrainment produced.
(*b*) Pressure drop across the plate.

For columns operating at reduced pressure the factor (*b*) is usually the controlling one, otherwise a pressure would be developed at a point where it particularly was not wanted, *i.e.* in the still at the foot of the column. For columns operating at or above atmospheric pressure the factor (*a*) usually controls the maximum permissible velocity, but another factor which has to be taken into account is the tendency of the liquid to foam, because the amount of foam affects the amount of liquid entrained at a given vapour velocity.

Foaming.

A survey of the recent theories of foaming has been given by Lewis.[1] There is no experimental connection between either the surface tension or the absolute viscosity of the liquids and their foaming properties. Foaming is dependent on the adsorption of solute at the gas–liquid interface. This explains the fact that pure liquids do not foam, while solutions do. With solutions the approach of two liquid surfaces meets with a resistance which tends to prevent the two surfaces merging, this resistance being due to the adsorption of solute at the surface. Hence there is a concentration difference between the surface film and the main solution, and this sets up forces which oppose the rupture of the bubble film. If this concentration difference becomes sufficiently great, the bubble may not rupture on reaching the surface, but may accumulate there with other bubbles, and so form a foam.

Working with alcohol–water mixtures and perforated plates, Kirschbaum [2] plotted the foam height against the liquid composition, and found that the height rose fairly rapidly to a maximum at 30 per cent. alcohol, and then slowly fell, until at about 75 per cent. alcohol it decreased more rapidly again. This foam height decreased on increasing the vapour

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velocity until at a velocity of about 2·3 ft./sec. it was independent of the alcohol concentration. This may be explained by considering the mechanism of bubble bursting. As soon as the bubble rises above the liquid level the solution begins to drain away from between the inner surface of the bubble and the upper surface of the liquid. The solution drains out, and the surfaces become thinner until the buoyant effect of the vapour is sufficient to rupture the retaining film. Examination of the viscosity figures for water–alcohol mixtures shows that the viscosity rises fairly rapidly to 30 per cent. alcohol, is a maximum at 50 per cent. alcohol, falls slowly to 70 per cent. alcohol, after which it falls off more rapidly. Hence the foam height is greatest over the region where the viscosity is the greatest. This is due to the slower rate of draining of the liquid between the surfaces for the more viscous solutions; hence there is a time-lag before the bubble bursts, during which time it is able to rise higher. On increasing the vapour velocity the buoyant effect of the vapour will be greater, and hence able to rupture a thicker film than before. The bubble will therefore burst sooner, resulting in a decreased foam height as found.

Kirschbaum [2] found that the efficiency at the top plates of a column was very high, but lower down, where the concentration of alcohol was about 30 per cent., it was much lower, owing to the increased foam height, and hence increased entrainment. On the other hand, at higher vapour velocities the difference in efficiency between the plates was not so marked, since at these increased velocities the foam height did not vary so much with concentration. By increasing the distance between the lower plates of this column, it was found that they became nearly as efficient as the top ones, thereby definitely showing that it was excessive entrainment that brought about this decrease in efficiency. Hence in the region of the column, where the conditions are such as to produce excessive foam, the plates should be kept farther apart.

The adsorption of one of the components at the gas–liquid surface also has an effect on the plate efficiency. Consider a mixture rich in the less volatile component B. The more volatile component A may then be regarded as the "solute," the mixture being a solution of A in B. When the solute concentrates at the interface, it is said to be positively adsorbed, whereas when it tends to concentrate in the body of the solution, it is said to be negatively adsorbed. From the point of view of foaming it is immaterial which occurs, for in both cases there is a concentration difference between the bulk liquid and interface which is all that is essential to produce foam. But from the point of view of exchange of material between vapour and liquid it is important. As the bubble rises through the liquid an exchange of material takes place with the liquid comprising the interface, some of B passing from the bubble to the interface and some of A passing from the interface to the bubble. If, now, the solute A is positively adsorbed, the interface is richer in A than is the main liquid. On the other hand, if A is negatively adsorbed, the interface is richer in B than is the main liquid. Therefore, in the first case there is a greater difference in concentration between the vapour in the bubble and the interface than in the second, and consequently a greater tendency to produce an exchange of material. Hence a higher efficiency will be obtained in the first case. It may be concluded, therefore, that the greater plate efficiency will be

obtained when the more volatile component of the mixture being distilled is positively adsorbed at the interface.

Free-space Column Velocity.

The values given in the literature for the maximum permissible free-space column velocities are somewhat conflicting. In many cases insufficient data are given regarding the spacing of the plates, etc. Peters [3] recommends a free-space column velocity of about 1·3 ft./sec. for water-alcohol mixtures. Carey [4] gives rather more valuable information on this subject. He states that the extent to which entrainment may be tolerated depends on the nature of the substances undergoing separation. In petroleum distillation, higher boiling-point components may be carried up the column as entrained particles, thereby imparting undesirable colour to the products. A very small amount of entrained coloured bodies will do great harm in this case, whereas if the only consideration were the effect on plate efficiency, a relatively much larger amount of entrainment would not appreciably vitiate the fractionating efficiency. Permissible vapour velocities appear to be almost independent of the mixture being distilled, provided it is not one which foams badly.

Experiments on the amount of entrainment produced by a given vapour velocity have been carried out by a number of investigators.[5, 6, 7, 8, 9, 10] Unfortunately, in most cases the experimental column used is so small and the spacing of caps, etc., so different from the usual commercial bubble-cap column that the results obtained will not be applicable to large-size column. By far the largest column used was that by Strang,[8] whose column was 3 ft. in diameter and contained twenty-seven bubble-caps per plate. In such a column, therefore, the effect of the walls of the column as spray catchers and the spacing of the caps would not be widely different from the same effects in a commercial column of, say, 10 to 15 ft. diameter. In all the experiments on entrainment the chief factors affecting it were found to be the vapour velocity up the column and the distance between the plates. Several other factors of design, such as the size of slots and depth of submergence, also have a slight effect.

Sherwood and Jenny [9] correlated their own entrainment results with those of other investigators [5, 6, 7] and concluded from the data available that the allowable vapour velocity from the point of view of entrainment was 4 ft./sec. at a plate-spacing of 12 inches. Strang [8] concluded from his experiments that the allowable velocity V was given by

$$V = \frac{1}{28{\cdot}8}\left(\frac{d_1 - d_2}{d_2}\right)^{\frac{1}{2}} . V_0$$

where d_1 = density of liquids, d_2 = density of vapour and V_0 had the value of 2·7 ft./sec. for 12-inch spacing, 5·1 ft./sec. for 18-inch spacing and 6·7 ft./sec. for 24-inch spacing, as will be seen from a plot of this data in Fig. 1. It seems probable that at higher velocities the column capacity would be limited by pressure drop rather than entrainment.

Consider the design of a column to fractionate a given quantity of material, *i.e.* given column capacity. Increasing the vapour velocity beyond the point necessary for adequate agitation will decrease the efficiency due to

increased entrainment, but will result in a decreased column diameter. In order to keep the entrainment down, it will be necessary to increase the distance between the plates, resulting in a taller column. Hence an economic balance will have to be made to decide between a taller and a broader column.

Having fixed the diameter of the column, the vapour velocity and the distance between the plates from considerations of the above and the required capacity of the column, the remaining factors of design should be such as to give the best efficiency under the said conditions of operation. Such factors affecting efficiency are well summarized by Carey,[4] viz :—

(*a*) Attention to the design and spacing of caps;
(*b*) Use of the greatest allowable depth of immersion of the caps;
(*c*) Obtaining good distribution of reflux liquid flow over the plate and preventing short-circuiting of liquid or vapour.

Vapour Up-take Area and Pressure Drop across Plate.

For columns operating at or above atmospheric pressure the pressure drop across the plate is not of paramount importance, but nevertheless it should be kept as low as possible. It is made up of :

(1) Head of liquid equal to height of liquid surface above the lowest open part of the slot;
(2) Contraction loss due to the passage of the vapour flowing through the up-takes. This factor is difficult to evaluate, but is usually obtained from the formula :—

$$h = u^2/2gc^2$$

where h = pressure loss in ft. of vapour flowing;
u = vapour velocity through up-takes—ft./sec.;
c = coefficient of value 0·3–0·6, which varies with the design of the plate.

Two points arise in considering means to keep the factor (2) as low as possible. Firstly, the up-take area must be as large as possible, in order to keep the value of u as low as possible. Secondly, expansion and contraction losses must be avoided in the passage of the gas through the up-takes and the cap by making the following areas the same : (*a*) Area of up-take; (*b*) area between top of up-take and top of cap; (*c*) area between outside of up-take and inside of cap.

An important point of design for minimum pressure drop, therefore, is one of obtaining maximum up-take area. Chillas and Weir [5] recommend that for large columns the up-take area should be 11–12 per cent. of the total plate area. Winkler and Koch [11] claim that with hexagonal caps a greater number to a given area can be provided, and moreover that the distance between the adjacent faces of all the caps is kept the same. It is also found that this construction provides a greater number of comb teeth, and thereby better ensures the breaking up of the gas and the more efficient deformation of the bubbles, through striking those emitted by the next adjacent cap.

Consider, therefore, the fitting of hexagonal caps round vapour up-takes of internal diameter 3 inches, which is a reasonable size. Assume also the thickness of the metal comprising the caps and up-takes to be 1/8 inch.

Then external area of up-take $= (3\frac{1}{4})^2\pi/4 = (10{\cdot}6)\pi/4$. But area ($a$) must equal area ($c$) as mentioned above, therefore internal area of hexagonal cap $= (9 + 10{\cdot}6)\pi/4$

$= 15{\cdot}4.$

Let length of side of hexagon be L.

Then area of hexagon $= \dfrac{3\sqrt{3}}{2} L^2 = 15{\cdot}4,$

whence $L = 2{\cdot}5$ inches. Since the thickness of the metal is assumed to be 1/8 inch, the external length of side of the hexagon is 2·65 inches. Allowing 1 inch distance between the faces of adjacent caps, the distance between the centres of two up-take pipes in the same row is 5·6 inches. Leaving room for liquid down-take pipes, it is possible to fit twenty-seven caps in a column of 36 inches diameter, as shown in Fig. 2. This gives an up-take area of over 19 per cent. of the column area, which is considerably higher than that recommended by Chillas and Weir,[5] and probably gives much reduced pressure drop. However, it is usually necessary to fit the caps into a column the diameter of which has been determined from the required capacity. If, therefore, the column diameter required was, say, 40 inches, it would be necessary to increase slightly the size of the up-takes and caps

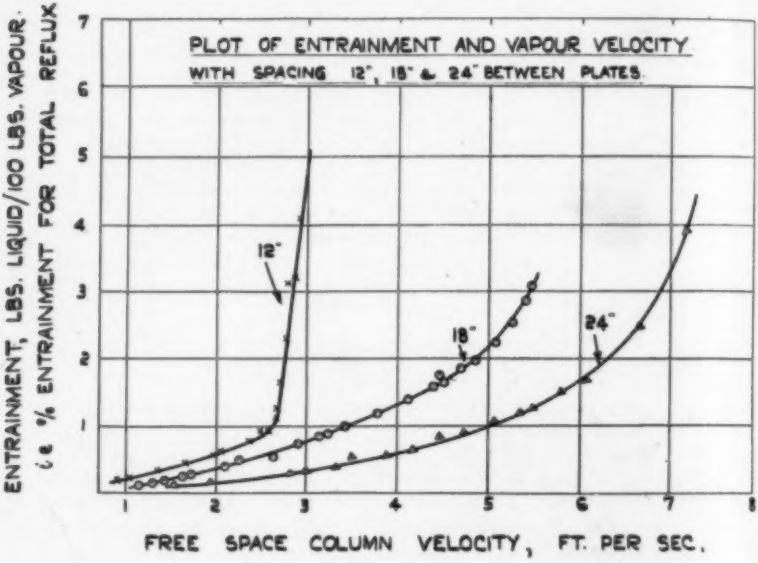
PLOT OF ENTRAINMENT AND VAPOUR VELOCITY
WITH SPACING 12", 18" & 24" BETWEEN PLATES
ENTRAINMENT, LBS. LIQUID/100 LBS. VAPOUR.
i.e. % ENTRAINMENT FOR TOTAL REFLUX
12"
18"
24"
FREE SPACE COLUMN VELOCITY, FT. PER SEC.

FIG. 1.

in order to fit them in, and this would probably slightly alter the value of the percentage area given above, but it would undoubtedly be of the same order.

The following results, denoting the pressure drop across a plate of the above design, were obtained by blowing air up it and bubbling it through water on the plate. The depth of opening of the slots was obtained by

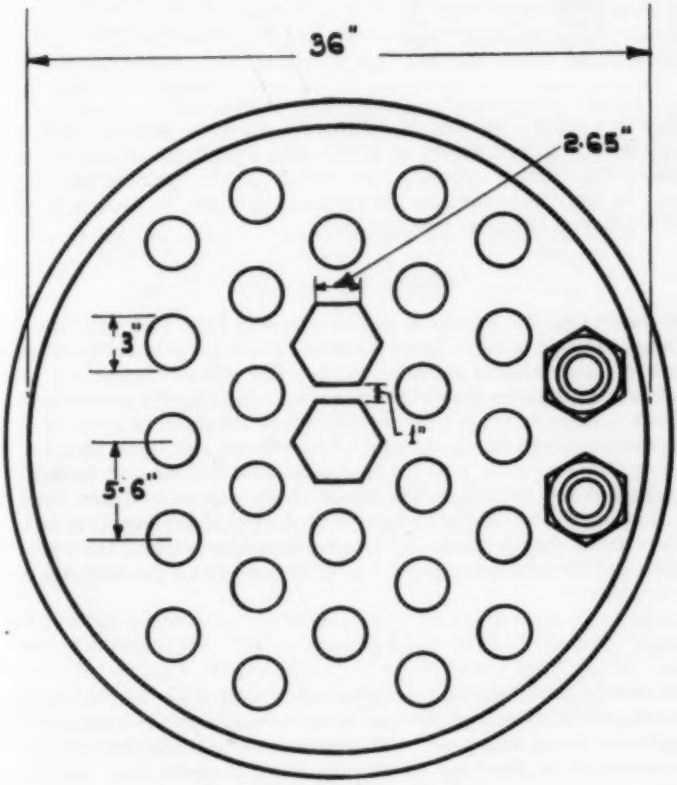

FIG. 2.

PLAN OF PLATE SHOWING 27 UP-TAKES.

enclosing a single cap in a glass cylinder and observing the opening. The caps were hexagonal, and contained four slots per side, each being 1½ inch long, 3/16 inch wide at the top and 3/8 inch wide at the bottom. Since at no flow of air the pressure drop across the plate is 0·85 inch, it is possible to calculate the amount of increased pressure drop due to the passage of the gas through the plate when the rate of flow of gas is increased. This is the observed total pressure drop less the sum of 0·85 inch and the depth of opening of the slot.

Velocity up Column (Ft./Sec.).	Total Pressure Drop (Inches Water).	Opening of Slot (Inches).	Pressure Drop due to Friction (Inches Water).
—	0·85	—	—
0·68	0·90	—	—
0·895	1·00	—	—
1·295	1·15	0·30	negligible.
1·628	1·30	—	—
1·880	1·40	0·52	0·03
2·160	1·55	—	—
2·29	1·60	0·63	0·12

Thus at a column velocity of 2·29 ft./sec. the total pressure drop across the plate is 1·60 inch water, of which only 0·12 inch, *i.e.* 7·5 per cent., is due to the friction opposing the passage of the gas through the cap. Hence, at the usual velocities the pressure drop due to friction is only a small fraction of the total pressure drop.

Height of the Caps.

To ensure that the vapour is bubbling equally from each cap, care must be taken to avoid a large liquid gradient, which persists even under conditions of most violent agitation, across the plate. Chillas and Weir [5] found that caps protruding above the level of the liquid produced such a gradient. They therefore recommend caps of the order of 2¼ to 2½ inches high, and these caps should be completely covered with liquid by arranging the overflow weir to be ¼ to ½ inch higher than the caps. The height of the caps will also determine the height of the vapour up-takes, since the area between the top of the up-takes and the top of the caps is to be equal to the area of the up-takes. If x be the distance between the top of the up-take and the underside of the top of the cap, and d the diameter of the up-take, then

$$x\pi d = \pi d^2/4$$

whence

$$x = d/4$$

Hence the height of the up-take pipes must be shorter than the height of the underside of the top of the caps by an amount equal to a quarter of the diameter of the up-take pipes. Allowance must be made, however, for the area taken up by that part of the cap which supports it to the up-take pipes.

Design of Slots.

Experiments by Carey [4] on the distillation of ethanol–water mixtures showed that optimum plate efficiencies due to intimate contact were obtained with slots 1/16 inch in width. Strang [8] also showed that such slots gave less entrainment than wider ones. The mechanism of the rate of bubbles rising in liquids has been studied by Bond,[12] and Owens.[13] Bond measured the rate of travel of air bubbles in viscous fluids (water glass and castor oil), and found that the velocity $v = \frac{1}{K}\left\{2/9\frac{(P^1 - P)ga^2}{\mu}\right\}$, where

P^1 = density of liquid, P density of gas, a = diameter of bubble, μ = viscosity of liquid, and $\frac{1}{K}$ = constant = 1·43. Thus the greater the diameter of the bubble, the greater is the velocity. Owens [13] investigated the conditions governing the size of the bubbles. He found that when the bubbles were allowed to form slowly one by one, the influence of the orifice diameter was very small. As the rate of flow of air was increased, a more rapid stream of bubbles was emitted, and they were of larger diameter; moreover, the larger the diameter of the orifice the more easily these bubbles seemed to coalesce into streams.

Experiments by the author confirmed these conclusions. Observations were also made on the amount of spray produced by blowing air through various orifices submerged under a head of 1¼ inch of water. The results were as follows :—

Orifice Diameter (Inches).	General Spray Height (Inches).	Droplets Height (Inches).
3/64	1½	none
1/16	2½	6
1/8	5	12
Four 1/16	4	9

Thus the four 1/16-inch diameter orifices (the area of which equals that of one 1/8-inch diameter) give rise to less splashing than the 1/8-inch diameter orifice, indicating that small slots in bubble-caps will give rise to less entrainment than wide slotted ones.

It was also noticed that there was a great difference in the behaviour of large and small bubbles on reaching the surface. The small ones were still very nearly spherical, but the large ones had flattened out, and hence on bursting were able to lift a large "skin" of water up into the vapour space.

Hence it is clear that slots as narrow as 1/16 inch are to be recommended for use in bubble-caps. Such slots could be made by sawing the cap. A reasonable distance between the slots would be 1/8 inch, thereby having one slot per 3/16-inch length of side of cap. Therefore for a length of side of 2·65 inches thirteen slots could be cut, making a total of seventy-eight slots per hexagonal cap.

Height of the Slots.

The minimum height of the slots must be such that at the maximum capacity of the column the total slot area available is in use. To allow for cases of sudden overloading, it is usual to leave a clear space of about ¼ inch between the bottom of the caps and the plate. The expression "slot velocity" has often appeared in the literature, being the velocity of the vapour calculated to be passing through an area equal to the total available area. In point of fact, this expression has no significance, for on increasing the amount of vapour passing through the slots, it is the slot area in use which increases rather than the velocity through the slots. By regarding the slot as an inverted weir, Rogers and Thiele [14] derived an expression for the depth to which a slot opened.

They found that for the rectangular slots the expression

$$V = 0{\cdot}51\,\frac{W}{144}\left(\frac{2g}{12R}\right)^{\frac{1}{2}}(h)^{7/4}$$

was valid.

Where V = volume flow through one slot—cu. ft./sec.
R = (density of vapour)/(density of liquid — density of vapour).
W = width of slot in inches.
and h = slot opening in inches.

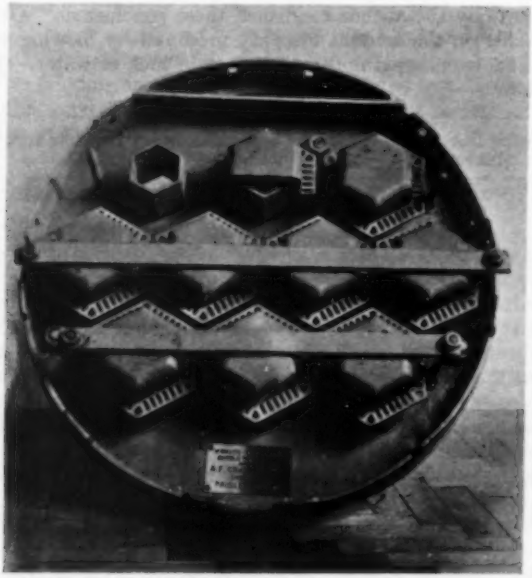

Fig. 3.

Hence h can be calculated for a column operating under given conditions, *i.e.* for the passage of V cu./ft. per second of vapour passing through the slot.

It must be realized that should the distance between the plates, and consequently the permissible vapour velocity of the column, be very large, the height of the slots might become too large compared with the height of the caps. In such a case, by increasing the slot width to 3/32 inch or 1/8 inch, the volume capable of being passed per unit height of slot would be increased, although the efficiency would be decreased slightly.

Intimate contact between vapour and liquid may be further increased by the use of suitable devices. Burke [15] designed a cap, illustrated in Fig. 3, to prolong the intimate contact by causing the vapours to travel farther in the liquid away from their point of exit from the cap. The cap was provided, above the slots, but below the liquid level on the plate, with a

circumferential horizontally extending flange, which stopped the vapours from rising to the surface immediately after passing through from the slots, and caused them to travel in the liquid to the outer perimeter of the flange before they could escape.

Othmer [16] recommended a cap in which the slots were cut tangentially-opposed, *i.e.* the streams of bubbles from two adjoining slots in the same cap were discharged against each other, thereby causing deformation, and ensuring active agitation by cross-currents in the liquid on the plate.

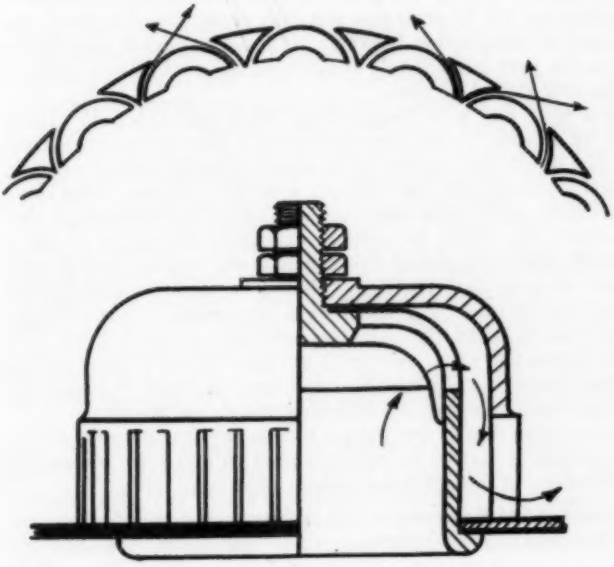

FIG. 4.

It is claimed that the use of such caps, one of which is shown in Fig. 4, reduces the number of plates required by 15 to 25 per cent.

DISTRIBUTION OF VAPOUR AND LIQUID.

This is another factor affecting the plate efficiency. The usual procedure in distillation columns is to have the downtake pipes attached to successive plates on opposite sides of the column, so that the liquid flows across one plate, down the overflow pipe and hence back across the next plate, the path of the liquid being baffled to avoid stagnant spots of liquid on the plate. This procedure has, however, the following objection :

Consider two successive plates A and B, A being above B. Let the composition of liquid flowing on to plate A from the plate above be x_0. While flowing across the plate A, this liquid is being fractionated, so that when it arrives at the down-take pipe its composition will now be x. On arriving on plate B its composition is still x_1, but after flowing across plate B it will

have reached a composition x_2. Hence on the side of the column containing the down-take pipe the difference in composition on the two plates is very small, while on the other side it is large $(x_2 - x_0)$. Consequently, as the vapour bubbles through the liquid, on one side of the plate there is only a small driving force to produce exchange of materials, and the average driving force over the plate may be compared with the average temperature drop produced in a parallel current heat exchanger.

The column should therefore be designed so that the driving force is comparable with the average temperature drop produced in a counter-current heat exchanger, *i.e.* by arranging the path of the liquid in such a way that the change in composition between the liquid on part of one plate and the liquid on the part immediately above it on the next plate is approximately constant over the whole plate.

Such a plate has been designed by Baker and Peters.[17] The plate is divided by a baffle, so that liquid flows round it in a counter-current direction. The liquid downspouts are inclined, instead of being vertically above one another throughout the column, with the bottoms of the downspouts also vertically above each other, but separated by a baffle from the tops of the downspouts. Also, to prevent excessive turbulence of the vapour, a few baffle plates are arranged vertically in the vapour space of the column.

Hence on each plate the liquid should be made to travel in the same direction and to pass by as many caps as possible. Care must be taken, however, not to make the path too tortuous, as this will set up a liquid gradient across the plate, and result in more vapour passing through some caps than others. Both Kirschbaum [2] and Brewster [18] found that plate efficiencies were increased by following the above procedure.

Thus it is seen that in designing a bubble-cap fractionating column there are a number of factors to be considered in order to obtain maximum plate efficiency at the optimum column capacity.

Department of Oil Engineering and Refining,
University of Birmingham.

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APPARATUS FOR THE DETERMINATION OF THE APPARENT VOLUME AND OF THE VOLUME OF VOIDS.*

By J. P. Buwalda.

The apparatus consists of three main parts: a glass vessel H; the top part K ground to fit into H; and the graduated tube L.

The vessel H is about 55 mm. high, and has an inside diameter of 35 mm. The ground rim is about 30 mm. high. At the bottom of H there is a three-way cock C (bore 5 mm.); one of its connections is joined to the levelling vessel P by means of a rubber tube. The other connection of the three-way cock C is joined by a tube to the bottom of the graduated tube L.

The top part K is ground to fit into the neck of vessel H. It is essential that the top surface of K should not be flat, but amply cone-shaped (for instance, with a top angle of 90°), so that, when H is filled with mercury, it is impossible for air to remain behind. Part K is further provided with a narrow rising tube with scale. At the top of this tube there is a cock A (bore 3 mm.), above which a short piece of wider tube is mounted. The narrow graduated tube has an inside diameter of 4 mm. and is 20 cm. long, so that its capacity is 2·5 c.c. This tube has a scale division in tenths of c.c. with a subdivision in 0·05 c.c. The zero point is at the top below the cock.

By means of a clip 9 with springs, the stopper K can be clamped around the vessel H. The graduated tube L, which is connected to the side-tube of the three-way cock C by means of a vacuum tube, consists of a glass tube, divided into 0·1 c.c., and with a 60-cm. scale reaching to 50 c.c. The zero point of the scale is at the top of tube L under the globe, while the end of the scale is at the same level as the graduation mark 2·00 of the scale on the narrow graduated tube and the top part K. The diameter of the globe should be about 70 mm.; at the bottom, tube L is provided with a cock D with a bore of 5 mm.

The levelling vessel P, which can be moved up and down along the guides, is connected by a tube with the three-way cock C, and is balanced by the counterweight 7.

To ensure convenient and safe transport, the whole apparatus is designed to be fixed into a case, which, when the apparatus is in use, can act as a stand. The top lid of the case can be put out of the way by turning it backwards, and then the front half placed on the back half by turning it on two hinges at the top and fastening by means of a latch and a hook. The front and back walls of the chest are now in one plane, forming a surface on which the whole apparatus is mounted ready for use, only the connecting tube between the three-way cock C and the levelling vessel P having to be fitted and the apparatus filled with mercury from the mercury bottle.

* Paper received November 6th, 1935.

Procedure in the Determination of the Volume of the Voids in Samples of Stones.

Two magnitudes of the sample have to be determined:

A. The apparent total volume of the sample;
B. The volume of the voids.

With the apparatus described, these two determinations can be made in succession on the same piece of the stone sample.

A. Determination of the Apparent Total Volume of the Sample of Stones.

1. Care is taken that the apparatus is perfectly clean and dry, that the ends of the graduated tube *L* and the side-tube of the three-way cock *C* fit as closely as possible and that the cocks *A*, *C* and *D* and the ground surfaces of *H* and *K*, after being sufficiently greased, fit tight.

2. The apparatus is placed on a horizontal plane, and tube *L* is erected vertically; cocks *A*, *D* and *C* should be open. The mercury reservoir *P* is moved up to the same height as the top part *K*, so that the bottom is on a level with the division *M*, which marks the end of the scale on tube *L* and which is on a level with the division 2·00 on the top part *K*.

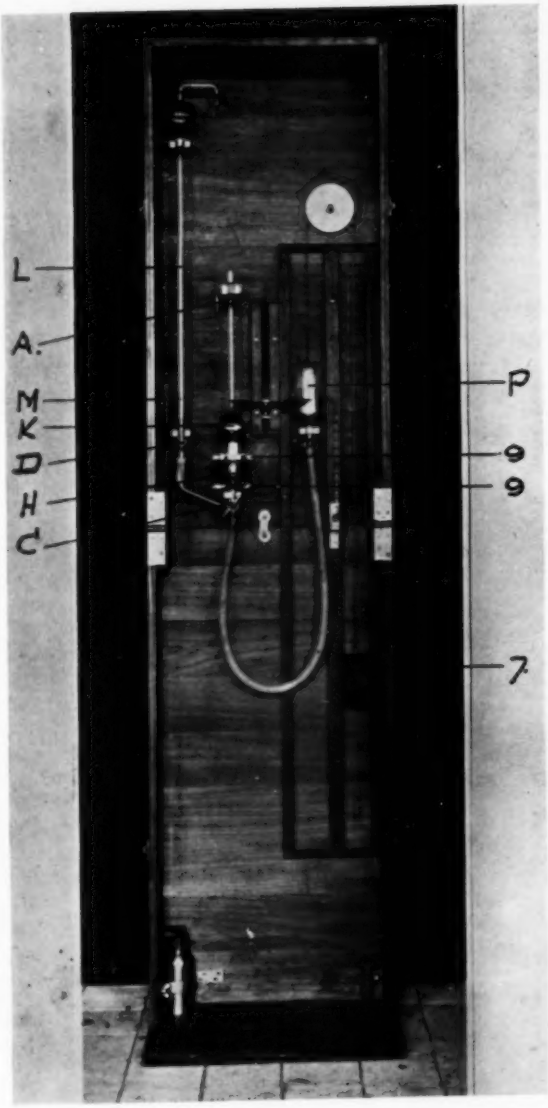
The reservoir can be fixed by tightening the clamping screw of the counterweight 7. The mercury reservoir *P* is now filled with mercury up to the division *M*. By moving vessel *P* up and down a few times, the air is driven out of the connecting tube, and then *P* is fixed so that the level of the mercury is on a line with the division *M*, cock *D* is closed and the rest of the apparatus is filled up to cock *A* by raising vessel *P*. Cock *A* is then closed, *P* is let down to the bottom, so that a vacuum is formed in vessel *H*, and the air escapes from the mercury and the tube. This is repeated until all the air has disappeared.

If *H* and *K* are entirely filled with mercury, cock *C* is so turned that vessel *H* is only connected with tube *L*. (Vessel *P* is fixed at about the level of cock *C*.) Cocks *A* and *D* are opened and some mercury is sucked from *H* into *L*; it is then allowed to flow back, and this is repeated a few times, so as to expel the air from the connecting tubes. Subsequently, some air is sucked into tube *L*, cock *D* is closed and, by cautiously opening this a little, sufficient mercury is admitted to *H* and *K* that the level in *K* is on a line with the division 2·00 on the top tube of *K*. (While this is done, cock *A* is open, and should be left open during this determination.)

Cock *D* is then closed and the position of the mercury in the graduated tube *L* is read and recorded.

3. The stone sample to be examined is weighed accurately to within 0·01 gram.

4. The top of *L* is connected with the suction pump, and by opening *D* sufficient mercury is sucked out of *H* that the edge of the ground joint rises above the mercury surface, care being taken that not the slightest amount of mercury can overflow from the top of the globe on *L* into the suction tube. Cock *D* is then shut and the connection with the suction pump is broken.



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5. The top part K is removed, the sample under examination is placed in vessel H, and K is replaced on the vessel.

6. Cock D is cautiously opened, owing to which the mercury from tube L flows down and again fills vessel H. At the moment when the surface reaches the division 2·00 on K, D is closed and the position of the mercury is read on the graduated tube L and recorded.

7. Cock D is opened, the mercury is sucked back into the globe of the graduated tube, D is closed, H opened and the stone sample is weighed once more. If the weight has remained the same, the difference between the two readings on the graduated tube indicates the apparent volume of the stone. If the weight of the stone has increased, this increase in weight, expressed in grams, is divided by 13·6, and the volume V of the absorbed mercury thus found is added to the determined apparent volume of the stone.

B. DETERMINATION OF THE VOLUME OF THE OPEN PORES PRESENT.

1. The sample used for the determination of the apparent volume is placed in vessel H, and this is closed off by the top part K.

2. Cock C is so turned that vessel H is connected with vessel P; this is raised until the mercury in K rises just above cock A, which is then closed.

3. Reservoir P is moved down, and after some minutes raised again, so that the mercury level in P is as high as that in K. The volume of air which is then under atmospheric pressure in the narrowed part of K is read and recorded.

If the samples are fairly large and have a considerable volume of voids, there is a possibility that, if the mercury reservoir is completely lowered during the first measurement, a quantity of air larger than 2·5 c.c. is liberated. It is therefore recommended to lower reservoir P only partly during the first measurement, and to ensure, by a preliminary reading of the volume of air, whether it is permissible to apply greater sub-pressure. With a view to the fragility of the apparatus, the graduated tube on the top part K has not been made longer.

4. P is raised a little above cock A, and this is carefully opened to allow the air to escape from the tube.

5. The manipulation of points 3 and 4 is repeated as long as a measurable quantity of air is liberated from the stone sample.

The volume of the voids is found by adding up the quantities of air collected, possibly increased by volume V found under item 7 of the determination of the apparent total volume.

The volume of voids expressed in percentages is found by dividing the volume of the voids measured by the apparent total volume of the stone sample and by multiplying this quotient by 100.

NOTE ON A LUMP OF ASPHALT FROM UR.

By R. J. Forbes.

The reader of this journal will remember a note on an asphalt ring from Ur of the Chaldees, which appeared some years ago.[1]

Sir C. Leonard Wooley, when excavating the site of Ur in 1934, found a big lump of asphalt embedded in what is known as the "Flood Layer."* It consists of an irregularly shaped mass with a roughly circular cross-section, tapering slightly from top to bottom, and appears to be a conglomerate of a number of individual pieces which have fused together, stratified in places by thin layers of mineral matter. The central portion consists of a core of mineral matter akin to that originally covering the whole. The core contains both large and small fragments embedded in it. In several places it has been possible to dig deep cavities in the sample by removing mineral matter without disturbance of the asphalt, the material removed being similar to that remaining in the main central core. These cavities are well defined in the photographs (Figs. 1 and 2).

The surface of the asphalt is speckled fairly uniformly by pockets of finely distributed mineral matter, the pockets varying in size from less than 1 mm. to as much as 10 mm. These pockets appear to persist throughout the mass, since they are evident in most of the larger fragments broken off during cleaning and in a section of the exhibit which was cut down by about 10 mm. to a plane surface. Also embedded in the asphalt are fragments of what appear to be wood, reeds or rush-like materials. The surface of the asphalt is covered with a somewhat glossy outer layer or patina, which flakes off readily, exposing a hard, friable asphalt.

The lump weighed about 10 kilograms (diameter 11 inches, height 5 inches), and during cleaning a sample of about 60 grams of fragments of asphalt and two samples of the mineral matter were collected. These two samples of mineral matter represent the dust removed from the large lump during cleaning, which had been sieved on a coarse sieve, and thus split up into two fractions merely to facilitate hand-picking of asphalt fragments. This mineral matter represents the material which forms what is known as the Flood Layer.

The asphalt sample was submitted to the action of a series of selective solvents, viz. pyridine and chloroform, whilst each extraction was carried on until the extract was colourless. Then the solvent was removed and washed out by a short extraction with benzene. The extracts were collected and the solvent was carefully evaporated on a water-bath and afterwards on an air-bath. It appeared that a large part of the asphalt was no longer soluble in even these powerful solvents, and because it was imperative to clean the mineral matter before examining it, it was decided to follow a somewhat unusual course.

After the CO_2 content of the remaining sample had been determined, it

* This specimen was presented to Mr. J. Kewley and exhibited by him at the meeting of the Institution of Petroleum Technologists on November 12th, 1935.

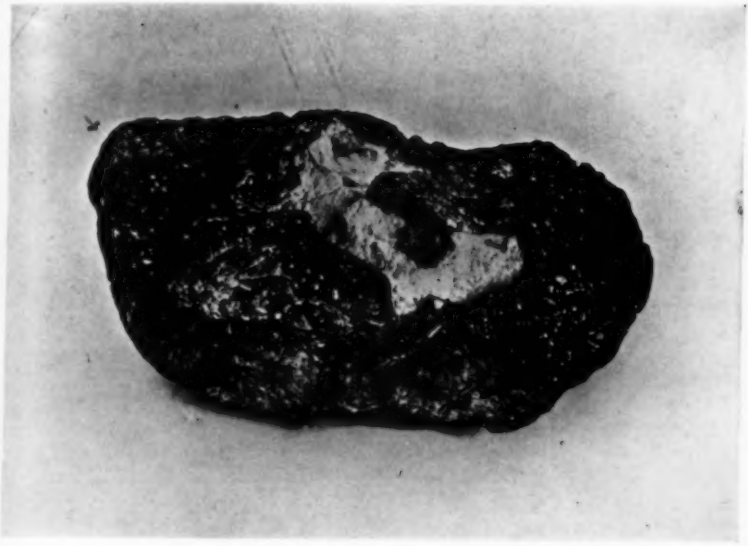

FIG. 1.

GENERAL VIEW OF THE LUMP OF ASPHALT FROM UR.

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FIG. 2.

A TOP VIEW OF THE LUMP OF ASPHALT FROM UR.

was subjected to a temperature of 350° C. on an air-bath for two days, in the course of which time the remainder of the organic material burned away slowly, leaving the carbonates unaltered, as was proved by checking this figure after the heating. The mineral matter was now ready for chemical and mineralogical examination. Unfortunately, the sample was too small to enable any analysis to be made of the vegetable remains, which were clearly distinguishable in the bigger lump. As far as our examination goes, they do not differ from those found in other asphalt samples formerly analysed.[2]

The composition of the asphalt sample is given in Table I.

TABLE I.

Composition of the Asphalt Sample.

Bitumen content :		
Soluble in pyridine, chloroform and benzene	39·5% by weight.	
Insoluble organic matter	37·0 „	
		76·5% by weight.
Mineral matter		23·5 „ „
Soluble Bitumen :		
Sulphur content	6·8%.	
Ash „	1·0%.	
Vanadium in ash	positive.	
Nickel „	faintly positive.	
Diazo reaction in bitumen	negative.	

Hard and friable bitumen giving a deep brown streak on porcelain.

The evidence shows that this sample is a specimen of the native asphalt so common in the numerous seepages on the right bank of the Euphrates. It probably comes from the region of Hit, where these seepages abound, and where bitumen was won from them for centuries. The mineral matter content is far too low for a mastic, and would seem to be merely the wind-blown desert dust collected by the bitumen in or near the seepage. (See Sample A, Table II.)

From the description of the general appearance of the sample, we must deduce that the lump was formed from smaller pieces thrown together, and perhaps pressed together, to remove, at least as far as possible, the water always included in these native asphalts from Mesopotamia. Sir Leonard suggested that it may represent the remains of a basket of asphalt ready for the preparation of a mastic for some form of constructional work. This would appear to be the case. The analysis, and the fact that we have here a complex of smaller lumps, not yet heated, with mineral matter unevenly distributed through the sample, would seem sufficient proof of this. On the other hand, we have no exact description of the way of collecting bitumen in those early times, and so we do not know whether the raw material was transported in baskets, though it would appear quite probable.

This sample must therefore represent the crude native asphalt called ESIR-LAḪ (" shining asphalt ") by the Sumerians, for the sample takes us back to the earliest period of Sumerian history, and this people dates its first dynasty from the times of the Flood, a natural catastrophe mentioned in the Bible as Noah's Flood. There is still considerable difference of opinion on the two following points :

1. Whether this barren Flood Layer (dividing the archaic remains from the historical period at Ur) is a product of the legendary Flood;
2. Whether we may conclude that similar barren layers found during the excavation of other old towns were deposited together in one deluge, or whether they represent local floods of different ages.

Even their date is still a matter of conjecture, as long as Mesopotamian chronology is not yet settled. Anyhow, we are safe if we adopt the lowest estimate for the Ur flood. The asphalt sample found therein may thus be dated back to about 3200 B.C.

It was already stressed that we possess no old Sumerian text on the winning of bitumen,[2,3] but we would like to direct attention to an Arabian text of an encyclopædia by the Persian author al-Qazwīnī,[4] who gives the following information on bitumen:

"There are two kinds of al-ḳîr (native asphalt). First comes the kind that oozes from certain mountains; then we have the kind that appears with water in certain pools. It boils with the water and as long as they remain mixed, the bitumen is soft; but if we separate them the bitumen hardens and becomes dry. It is collected by means of mats and thrown on the shore (of the seepage). Then it is brought in a kettle under which a fire has been lit, the sand is dissolved (?; mixed) and a certain amount added, and a mix prepared by constant stirring. When the mix is ready, it is poured on the floor, where it cools and hardens. Ships and bathrooms can be waterproofed in this way."

There is no doubt that this description of the bitumen industry of Mesopotamia in the middle of the thirteenth century shows that the old tradition lived on, for, as we know, this local industry is still flourishing,[5] and bitumen-coated "guffah" are still used for river-transport. The Sumerians clearly distinguished the different native asphalts from the mastic prepared therefrom, calling the latter ESIR-É-A ("house asphalt"). Here again we can find a proof that this sample was not a mastic, for there are two points in which asphalt and mastic differed in those times—namely, in the price and in the form in which they were sold.

If we compare different contracts in which we read about bitumen, we are struck by the fact that the mastic is always sold by volume—by the "Gur," the ancient measure for grain, beer, etc. Such is the evidence of ancient texts from the very same Ur.[6] Crude asphalt is always sold by weight, by the "mina" or "shekel," as were metals and other solid commodities. This means that the mastic was prepared by heating the crude asphalt and either selling it in these melting vessels (probably earthenware) or in the form of cakes, just like the modern mastic.

At the same time, the custom seems to have been to prepare the mastic on the spot, as contracts mentioning mastics are not very frequent, and usually mention only small quantities when compared with those calling for crude asphalt.[7] The price of the mastic is something like double that of crude asphalt, which may be explained by the shortage of fuel in a treeless country like Mesopotamia.[3]

Summing up all the evidence, we come to the conclusion that the sample is a lump of crude Hit asphalt which, as Sir Leonard supposes, may have

been left over from some building activity. The analysis shows that the bitumen has hardened considerably—why is not clear. Other samples of ancient mastics did not show this feature; they were always completely soluble in pyridine. Perhaps the explanation lies in the damp position and the constant change of the water-level in the Flood Layer, though such hardening has not been noticed in other mastics from other parts of the country,[2] which were also exposed to very damp conditions.

The analytical data collected on the mineral matter from this sample are given in Table II. There are several points of interest in these figures.

TABLE II.

Composition of the Mineral Matter.

	A. Mineral matter extracted from sample.	Mineral matter adhering to sample.	
		B. Coarse fraction.	C. Fine fraction.
	Per cent. by weight.	Per cent. by weight.	Per cent. by weight.
Screen analysis :			
On 10 # sieve	2·7	3·6	—
,, 20 ,,	3·3	9·4	—
,, 30 ,,	2·4	6·3	0·8
,, 40 ,,	2·9	6·4	2·8
,, 50 ,,	4·0	4·2	3·3
,, 80 ,,	5·3	8·0	24·6
,, 100 ,,	1·0	0·4	0·6
,, 200 ,,	9·8	22·3	26·8
Particle size :			
74–40 μ	20·3	32·7	16·6
20–40 μ	18·8	1·4	12·7
5–20 μ	11·5	1·0	6·6
0–5 μ	18·0	4·3	4·2
Chemical analysis :			
SiO_2 content	43·9	39·2	39·2
CaO ,,	13·7	15·2	15·2
CO_2 ,,	8·5	10·4	10·6

Mineralogical Analysis.—The general composition of these three samples is the same; they consist mainly of quartz and calcite, with smaller percentages of felspar and muscovite, also a fairly high percentage of a limonite-like material. Sample A contains the least calcite of the three.

The residues obtained by the heavy mineral analysis show that all three samples are essentially similar, being characterized by the Augite–Hornblende–Epidote association.

First of all, they show us that though the mineralogical character of the three samples does not point to any marked difference, the mineral matter extracted from the asphalt is very much finer. Of course, no great importance should be attached to the screen analysis of conglomerates like these samples, because during the test they disintegrate wholly or partly into the original particles. But the dust from sample A is much finer than the two samples from the Flood Layer, if we reckon only the very finest particles below 20 μ. These have the dimensions of the common clays,

and if therefore the wind-blown dust in the asphalt (sample A) is different from the mineral matter on the outer layers of the lump (samples B and C), the finest particles must have been washed or blown out of the latter.

For there is no reason why there should be any intrinsic difference. Sands from many spots in Mesopotamia, from the desert, river-bed, and river-bank, were examined, and they all show the same characteristics of the common desert sand, which in turn is derived from the erosion of the Cretaceous ranges on the north and south borders of the country. None of these samples differs very much from this wind-blown sand; the grading is characteristic for æolian sands which all have their main fraction within rather narrow limits (here roughly 150–40 μ).

Secondly, for the very reason that these sands differ only in minor points, it is extremely difficult to make out whether they are fluvial, marine or æolian deposits. It is interesting to read the analysis of samples of the Flood Layer and similar barren layers excavated in the ancient town of Kish; the results of which examination by V. Malycheff were published by Watelin.[8] These samples proved to be very rich in calcite and muscovite, and contain much less quartz than the usual sand from other countries. On the other hand, microscopical examination of the fossils proved that they contain mostly Cretaceous foraminifera. No characteristic marine or fluvial fossils were found, which again proves that all these Mesopotamian deposits have their origin in the desert sand which may have been transported by the rivers (or by the wind) to a secondary spot. Malycheff found sulphates and chlorides in the water-soluble part of the sands, a fact which we were able to confirm.

We must therefore point out that as these "Flood Layers" which have been found in several excavations in ancient Mesopotamian towns are not at all characteristic clay or sand deposits differing from the present desert sand, it will be difficult to decide whether their origin is fluvial, marine or æolian on the strength of some chemical or mineralogical analyses only, and the local conditions (topography, etc.) should be taken into account to decide this point.

The author wishes to thank Dr. Fulcher and Mr. Buwalda for their kind help in collecting the analytical data, and the Bataafsche Petroleum Maatschappij for permission to publish these notes.

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RUMANIAN BRANCH.

NINTH ANNUAL DINNER.

THE Ninth Annual Dinner of the Rumanian Branch of the Institution of Petroleum Technologists was held at the Piccadilly Restaurant, Ploesti, on December 7th, 1935. The Chair was taken by Mr. Percy R. Clark (Chairman of the Branch), and the guests included Dr. Hubrecht, the Dutch Minister; Mr. Harrison, the American Minister; Professor Dr. Leon, Under Secretary of State for Industry and Commerce; Mr. C. Alimănisteanu, Vice-President of the Senate; Mr. Cezar Popescu, Director General of Commerce in the Ministry of Industry and Commerce.

The Toast of "His Majesty King Carol the Second of Rumania" was loyally honoured.

MR. PERCY R. CLARK, in addressing the gathering, said that the year 1935 marked a new era in the petroleum industry, having brought a distinctive upward turn of the economic curve after what had been the worst slump the industrial world had ever known. It also marked the beginning of the gradual consolidation of the position of the petroleum industry into one of sound and healthy development. Since its inception that industry had been somewhat the spoilt child of the world's industries, having never been able to find enough oil to satisfy demands. This state of affairs was illustrated by the metaphor "to strike oil," an expression symbolizing the sudden acquisition of wealth.

Consequently, when exceptional conditions in 1930 brought the petroleum industry to a state of productivity greater than the market requirements, there were some who considered that disaster had overwhelmed the industry. They spoke of the hardship of having to limit production, apparently not realizing that every other industry had had to do this for many years.

With the gradual recovery from the crisis, the petroleum industry had commenced reconstruction on the basis of always adjusting supply to demand, and it was obvious that it would come through fortified and strengthened.

MR. WILLIAM BOLTON, in proposing the Toast of "Our Guests," referred to the honour conferred on the Branch by the presence of so many distinguished guests.

MR. J. L. CHAILLET, in proposing the Toast of "The Petroleum Industry in Rumania," said that, reviewing the progress made in Rumania during the last ten years, it could be said that history repeated itself. Until 1926 the industry had been very backward, but at about that time new ideas had been imported, and the recognition by the local companies of the advantages of rationalization, standardization and unification had enabled the industry to produce more oil in less time and at a cheaper cost.

Unfortunately, as fast as oil production rose in Rumania, so it did also in foreign fields, and there had always been the vigilant eye of the taxing authority. Although there are only about 30,000 persons engaged in the Rumanian petroleum industry, the result of their toil was that the State received a yearly income of some six to eight milliard Lei.

The internal consumption of oil products in Rumania was less than one-fifth of what was produced. There was therefore no need for Rumania to consider costly methods of extracting oil from coal or shale to safeguard home requirements, and the potentialities were such as to make the future optimistic.

PROF. DR. LEON, in reply, expressed the regret of Mr. Costinescu, the Minister of Industry, at being unable to be present. He said that the purposes of the Institution were the development of collective interests and would, he hoped, find a means of a happier collaboration between the technical men and the State organizations for the rational exploitation of new petroleum reserves.

MR. C. ALIMĂNIŞTEANU proposed the Toast of "The Institution of Petroleum Technologists," and MR. E. C. MASTERSON, in reply, said that a technical institution was never more necessary than at the present time. The Institution of Petroleum Technologists offered good opportunities for the exchange of information, and the discussions which followed the reading of papers were most valuable.

The subjects of general interest to the petroleum technologist were becoming more and more scientific, and technical men all over the world were continually studying the problems which arose.

Geological interpretation of surface data was sufficient when drilling in the Rumanian foothills, but in the plains it was necessary to make geophysical surveys. The art of drilling straight holes was an aid to the reduction of bad fishing jobs, and the study of drilling muds had greatly reduced the number of holes lost.

Developments in refinery practice offered plenty of scope for the engineer and the chemist, and polymerization was a general topic at present.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

BURMA BRANCH.

A meeting of the Burma Branch of the Institution of Petroleum Technologists was held on March 22nd, 1935. An abstract of the paper which was presented is given below :

DRILLING AND FISHING UNDER PRESSURE AT MASIMPUR, ASSAM.

By P. Evans, assisted by B. R. Emrick.

The Masimpur area in Assam presents a combination of drilling difficulties which are probably not exceeded anywhere else in the world. The principal troubles are :—

(i) heaving and squeezing shales,
(ii) high-pressure water and gas sands,
(iii) low-pressure zones in which circulation is liable to be lost,
(iv) steep dips,
(v) hardness of the rocks.

In an attempt to overcome these difficulties a Doheny Stone pressure-drilling equipment and hydraulic table were installed, and the well started with a 30-inch hole. Although many difficulties were encountered, the first 3000 feet were drilled by ordinary methods, and it was not necessary to go under pressure. Thereafter high-pressure sands were encountered, which made it necessary to use either heavy mud or surface pressure. Most of the drilling from 3000 to below 5000 feet was carried out with an unweighted mud and a surface pressure varying from 300 to 1300 lb. per sq. in. Subsequently, pressure increased, and it became essential to use weighted mud in conjunction with the surface pressure. The bottom-hole pressure at the present time is estimated at very nearly 7000 lb. per sq. in., and at times it has been necessary to have mud weighing almost 150 lb. per cu. ft. in the well.

At a depth of 5720 feet, after drilling through a great thickness of squeezing formation, a very soft shale was encountered, and the drill-pipe froze. Nearly two months were spent in recovering it. As it seemed most undesirable to permit any reduction of pressure except as a last resort, it was thought that an attempt to shoot off the bit would be the best means of regaining circulation, in which case the necessary hydrostatic pressure at the bottom of the hole could be obtained by using extremely heavy mud. This attempt failed owing to the difficulty of shooting with improvised equipment. The drill-pipe was eventually recovered by backing-off, washing-over and cutting out short lengths, and

after complete recovery of the fish it was found that the attempt at shooting had been almost successful.

Drilling then proceeded through squeezing formation. Unfortunately, a second fishing job occurred in circumstances which were an almost exact repetition of those attending the first fishing job. In this case the drill-pipe was backed off at the safety-joint, but immediately froze, and backing-off, washing-over and cutting-out were undertaken; but progress was interrupted by the freezing of the wash-over string, and at the present time fishing operations are directed towards the removal of the remaining portion of the wash-over string. During the whole of these operations the hydrostatic pressure at the bottom of the hole is kept as nearly constant as possible.

It is proposed to discuss briefly the difficulties encountered during drilling under pressure, and to pay most attention to the question of fishing under pressure, with the object of inviting discussion on methods of pressure-drilling, and particularly of fishing under pressure, as very little indeed has been written on fishing jobs in pressure-drilling.

SOLVENT REFINING.

THE following written contribution to the discussion on Solvent Refining has been received from Mr. F. E. A. Thompson :—

The increasing use of solvent processes in general refinery practice, particularly in the manufacture of high-grade lubricants, has emphasized the need for some reliable method for comparing solvent efficiency in order to distinguish between the various processes now available.

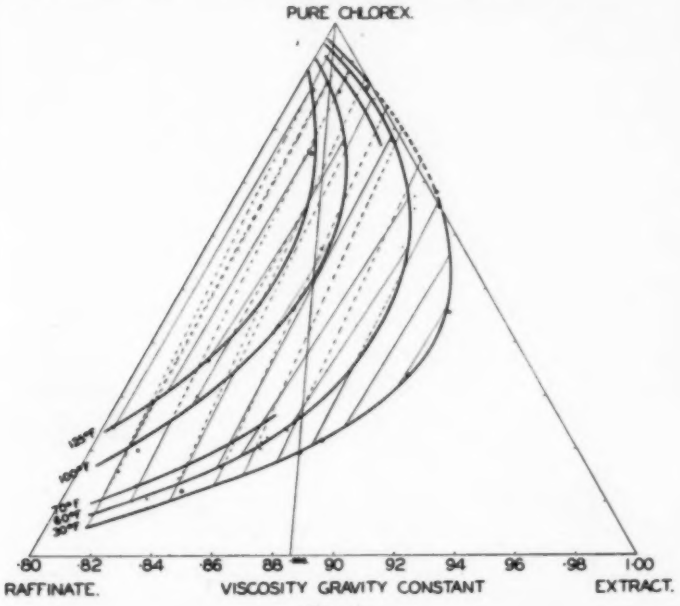


FIG. 1.

None of the three papers presented at the 168th General Meeting of the Institution,* however, attempts to differentiate between the relative efficiency of the processes described, and the confusion which exists to-day due to the lack of correlation of published results in the technical literature, is typified by the suggestion made during discussion that " all single solvent processes are about equal." It is perhaps only natural that the inventors of each solvent process should exert themselves primarily to demonstrations of the wide range of application of their particular solvent process to different types of charging stocks, but the result has been that little information is available regarding the treatment of the same charging stock with different solvents.

* See pp. 49–98.

The application of triangular graphs to the study of solvent refining gives a very clear picture of the effect of the various factors affecting solvent treatment, and enables the relative efficiency of the different solvents to be accurately assessed. It is unfortunate that in the admirable exposition of triangular graphs put forward by the authors of the third paper, no mention should have been made of what is probably the chief usefulness of these graphs, *i.e.*, determination of relative solvent efficiencies.

In this respect, Figs. 1 and 2 give a series of equilibrium curves for the same base stock (a distillate lubricating oil of 0·886 V.G.C. and 1235 secs. viscosity Redwood I at 100° F.) for chlorex and phenol over a range of

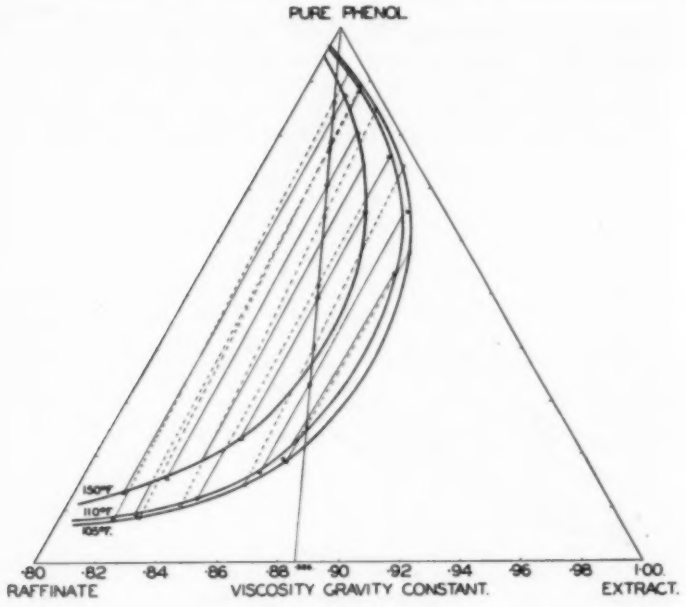


FIG. 2.

operating temperatures usually employed in practice. Similar series of curves may be prepared for any desired solvent and base oil.

Ferris, Birkhimer and Henderson (*Ind. Eng. Chem.*, 1931, **23**, 753) have published results of numerous experiments using a variety of solvents on the same base stock, and certain of their results are plotted in Fig. 3. The accuracy of their analyses for the more paraffinic raffinates is hardly sufficient for this method of representation, as is seen by the deviation between the experimental figures and the curves showing the estimated true relationships; but the analyses of the extract phases show better agreement.

Certain general conclusions regarding solvent treatment are obvious from an examination of curves such as those indicated :—

1. For any given solvent, the most naphthenic extracts are obtained by operating at the lowest possible temperatures.

2. For any given solvent, the production of high-quality raffinates is favoured by operating at increased temperatures.

3. For any efficient solvent process, the yield of raffinate (of any definite quality) is determined solely by the quality of the extract produced. Hence the maximum yield of raffinate obtainable from a given stock will be obtained by that process which yields the most naphthenic (worst) extract.

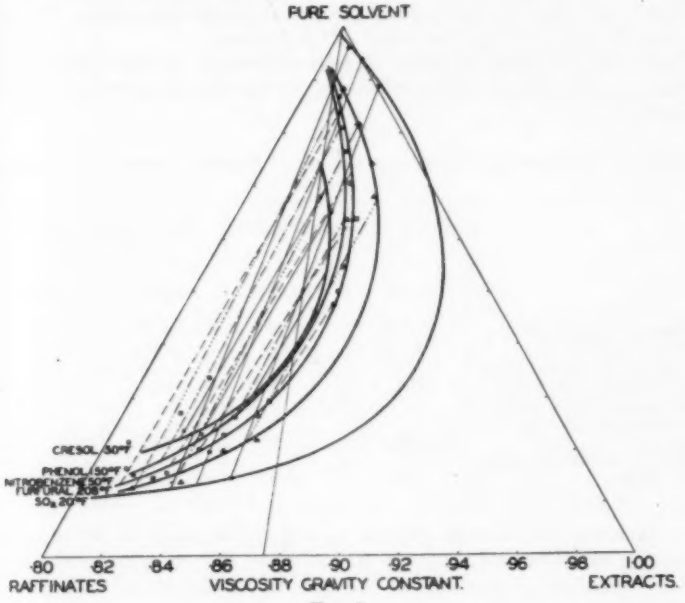


FIG. 3.

4. The advantages of maintaining a temperature gradient throughout a counter-current system are :—

(*a*) reduction of the amount of solvent required, and/or

(*b*) a reduction in the number of counter-current stages required to achieve a given separation into raffinate and extract of the desired qualities.

Since in practice it is not necessary to produce the highest quality of refined oil possible from a given starting stock, but only a raffinate of some definite quality (say 100 Viscosity Index), the choice of the best solvent process will be governed by such factors as :—

1. The most naphthenic extract obtainable at practical working temperatures. This will determine the maximum possible yield of raffinate.

2. Number of counter-current stages and volume of solvent necessary.

The above conclusions are exemplified by the following : The minimum operating temperatures for chlorex in commercial plants appears to be about 75° F., despite the fact that much greater yields are theoretically possible by operating some stages of the plant at lower temperatures (*i.e.* 30° F.). This limitation is mainly due to the slow separation rates of chlorex–oil mixtures containing large quantities of extract resins, etc., at lower temperatures.

Phenol is limited by its melting point to temperatures above 105° F., the usual minimum being about 110° F. in practice.

Under these conditions there is little difference between phenol and chlorex on grounds of solvent efficiency, as the figures given in Table I indicate.

TABLE I.

Comparative Estimates for Phenol and Chlorex as Selective Solvents, Derived from Figs. 1 *and* 2.

	Medium-Grade Raffinates (0·850 V.G.C.).		High-Grade Raffinates (0·816 V.G.C.).	
	Phenol.	Chlorex.	Phenol.	Chlorex.
Extraction Temperature .	110° F.	70° F.	110° F.	70° F.
V.G.C. of extract . .	0·972	0·966	0·972	0·966
Maximum theoretical yield of raffinate. % by vol.	70·5	69	54·7	53
Approx. number of perfect counter-current stages required	less than 1	1	2½	4
Volume % solvent required on charge . . .	137	138	190	153

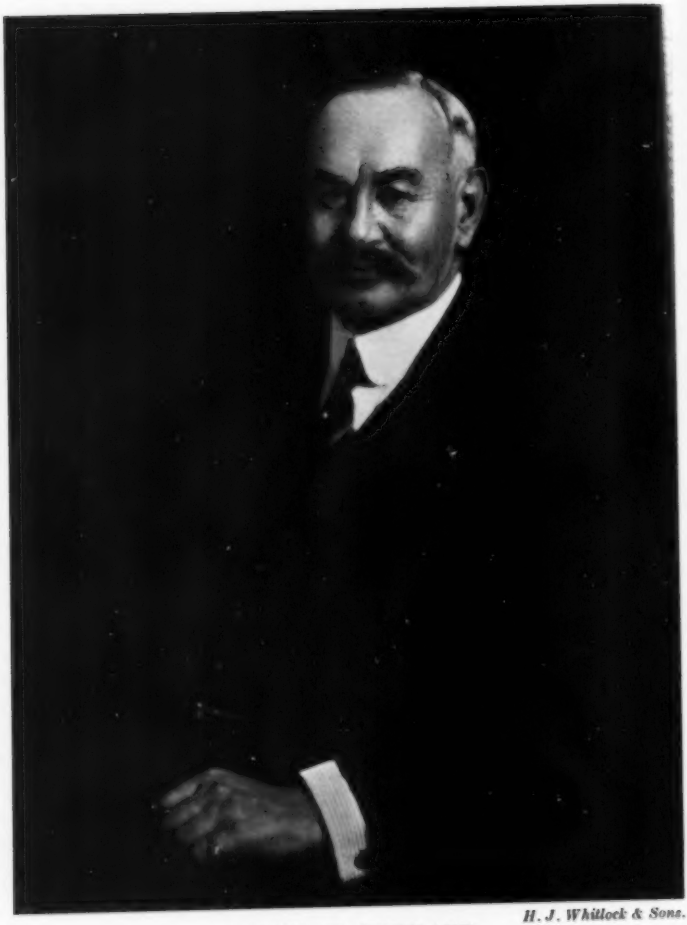
If, however, the results plotted in Fig. 3 be assumed to represent operating conditions for the respective solvents, then very different results will be obtained depending on the solvent employed, as indicated in Table II.

TABLE II.

Comparative Estimates for the Production of a 0·840 *V.G.C. Raffinate with* SO_2, *Furfural, Nitrobenzene, Phenol and Cresol, Based on the Results of Ferris, Birkhimer and Henderson.—See Fig.* 3.

V.G.C. of Starting Stock = 0·8745.

	Liquid SO_2.	Furfural.	Nitro-benzene.	Phenol.	Cresol.
Extraction temperature . .	20° F.	208° F.	50° F.	150° F.	50° F.
V.G.C. of most naphthenic extract obtainable at extraction temp. .	1·015	0·939	0·912	0·905	0·891
Maximum theoretical yield of 0·840 V.G.C. raffinate at extraction temperature	80·3%	65·2%	52·1%	47%	32·4%
Approx. number of counter-current stages required	2½	1½	less than 1	1½	1½
Volume % solvent required on charge	138%	100%	127%	138%	110%



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ARTHUR W. EASTLAKE.

[*To face p.* 193.

ARTHUR W. EASTLAKE.

An Appreciation.

When the idea of an Institution of Petroleum Technologists was first put forward by the late Sir Boverton Redwood, it was only natural that he should call upon his colleague, Mr. Arthur W. Eastlake, to assist him in bringing that idea to fruition. The vast amount of work which Mr. Eastlake devoted to the preliminary negotiations and planning is fully known only to those few persons who were associated with Sir Boverton in forming the Institution.

To a much wider circle Mr. Eastlake is known for the services which he has rendered to the Institution as Honorary Secretary, a position which he has occupied since 1915. In order that some tangible recognition might be made of his valuable services in the conduct of the Institution's affairs, a fund was instituted and a presentation made to Mr. Eastlake on the occasion of the Annual General Meeting, March 1936, conveying the good wishes of the members.

J. C.

To the President, Council and Members of the Institution.

GENTLEMEN,

I wish to express to you all my thanks for the generous expression of your appreciation of such services as I have been able to render to the Institution. It has been one of the great pleasures of my life to act as its Honorary Secretary.

When the Institution was founded in 1914 few of us could foresee the importance and the magnitude to which it would subsequently grow. My pleasure in its growth has, however, been exceeded by the happiness I have found in my numerous friendships with the members of the Institution. To all of them I express my thanks for their generous testimonial.

Yours sincerely,

ARTHUR W. EASTLAKE.

PRESIDENTIAL ADDRESS.

By Sir John Cadman, G.C.M.G., D.Sc.

It is only a year ago that the British nation was preparing, with gladness of heart and thankfulness, to celebrate the Silver Jubilee of its King. Those of us who were adult during the whole of the reign cast back our minds, first to the troublous years between 1910 and 1914; then onwards to the cataclysm of war; through the socially, politically and economically disturbed post-war period, to the early months of 1935. It was borne in upon us that, together, the King and the nation had faced, endured and surmounted many great trials.

Nevertheless, it could not be absent from our thoughts that the King's reign, although it was marked by violent happenings, was also a period of much development and progress in the sciences and arts of peace. In many of the activities which form part of our national life, the contrast between 1910 and 1935 revealed changes which rarely happen in so short a span as that of a generation. It was as though we had passed from one age to another in a single brief step.

This feeling was not confined to any one industry or one aspect of life, it was common to many phases; and there was a remarkable unanimity in the manner in which scientific bodies, our industries, the press, and the nation at large contemplated the changed features of our economic and social structure. Hitherto, we had been so concerned with the heaped-up troubles of the moment that we had been unable to stand aside and view the past in true perspective. We had not realized that we had cause for satisfaction. We had not thought that in living during King George's reign we had been participants in what will assuredly be one of the stirring times—the "spacious days" of future history. But, early in 1935, the realization and the thought came to us; and we prepared, in gladness, to celebrate the completion of an era—little knowing that in but a few months our gladness would be sharply transmuted into grief.

A year ago, it was right that our thoughts should be turned towards the past. To-day, however, we are on the threshold of a new reign. Our interest lies forward, not back—in the future and its probable developments rather than in achievements which are already a part of history.

No one, of course, can prophesy what will have occurred in twenty-five years' time; but I propose to open this first year of the Institution's activities in the reign of King Edward VIII by making a brief survey of present tendencies in affairs with which the Institution's members are

concerned, leaving it to posterity to decide whether, during our second generation, we have upheld the traditions established by the first.

Geophysics.

The notable successes of seismic reflection gives that method of exploration the first place in any consideration of the trend of future developments in applied geophysics.

The reflection method was originally developed for exploring the deep salt-dome structures in the Gulf Coast areas of Texas and Louisiana. The important results achieved by the method in these areas led to its wide adoption in other regions and countries.

Two different methods of reflection surveying have been developed in America. These are the correlation method and the dip method.

With the correlation method an attempt is made to identify the same reflecting horizons over the whole area to be explored; and from this information an underground contour map is constructed.

In many areas considerable difficulties are experienced in correlating the reflecting horizons. The dip method, which is in general use to-day in the Gulf Coast area, was designed to avoid these difficulties. No attempt is made to correlate the reflecting horizons, but the seismic detectors are arranged to give a measure of the dips of the horizons. From these dips a general picture of the structure is derived.

The older refraction method of geophysical surveying has lost ground on account of the great cost of operation and of its inability to indicate the presence of comparatively small structures at great depths. On the other hand, it is believed the refraction arc method will retain priority in initial exploratory work on anticlinal structures such, for instance, as those which exist in south-west Iran.

One of the most difficult problems presented in modern seismic exploration work is that of discriminating between impulses of different degrees of sharpness. The amplifiers have to be designed to give selective amplification to the sharp reflected impulses, and special filtering circuits have to be incorporated to suppress unwanted disturbances. This problem has not been completely solved, and further research is needed.

Attempts are also being made to simplify the seismograms. One method consists in using multiple detectors, suitably spaced over the ground, which effect some suppression of the slower surface waves and enhance the weak reflection impulses. Another method uses multiple explosions of small charges at varying distances and depths.

The use of multiple receivers and explosions is, in many respects, similar to that of multiple aerials and transmitters in wireless beam telephony.

During the last two years interest has revived in the gravity method of geophysical exploration, owing to the successful design of static gravity meters for field use. For these instruments a sensitivity of about one part in ten million is claimed. This corresponds to the change of gravity in rising one foot from the earth's surface. The gravity meter promises to be useful for conducting initial exploratory work, and it is believed that there will be extensive use of the instrument for this purpose in the next few years.

Geology.

In matters of geology members of the Institution will doubtless watch with much interest the exploratory activities now taking place in Great Britain.

Indications of petroleum have long been observed in various districts in Great Britain, and have been reported upon from time to time in H.M. Geological Survey Reports. Of these indications, the most widespread known to early investigators were associated with strata of Carboniferous age. A considerable number of seepages had been met in coal workings in the Midlands and in shale mines in Scotland, and the outcropping Carboniferous limestone in the Pennine Range contains a number of impressive instances of petroleum residues. It was this evidence which directed the investigations of 1918 and onwards when H.M. Government, through Lord Cowdray's organization (S. Pearson & Co., Ltd.), endeavoured to ascertain by the drill whether petroleum existed in this country in commercial quantities.

The drilling campaign during the years 1918 to 1922 had Carboniferous reservoir rocks as its sole objective, and the results were singularly disappointing. Most of the wells were located under favourable structural conditions; but, of the eleven wells drilled, the Hardstoft well alone achieved a modest measure of success. It is still producing small quantities of paraffin-base oil containing some 30 per cent. of lubricating oils.

The origin of this source of oil has never been determined.

For many years past members of the geological staff of the Anglo-Iranian Oil Company have been working on the problem as to whether oil may be presumed to exist in Great Britain in significant quantities, and in their researches they have covered a much wider range of investigation than that undertaken 16 to 18 years ago.

Whilst it is still felt that in certain areas the chances of discovery in the Carboniferous cannot be ignored, recent work tends to indicate the existence of favourable conditions in other zones, previously unexplored, where either the Permian or the lower Cretaceous and Jurassic

would constitute the main drilling objectives. The oil possibilities in these zones fall within separate and unrelated geological provinces between which no direct comparison can be made.

As a result of these investigations, and following on legislation which has enabled work to be carried out in a systematic and orderly manner, licences have now been granted.

In passing, I think it would be not inappropriate if I stated that, in my view, much credit is due to the Petroleum Department of the Board of Trade for the part they have played in modernizing our petroleum legislation on sound and sensible lines. Incidentally, this Institution also can take some small measure of credit to itself, seeing that a Committee of the Institution was asked to give the Department its general views on this subject.

Work on the areas which have been licensed is now in progress, and very shortly deep drilling will begin on certain selected structures.

It is, of course, quite impossible to forecast what will be the result of the search which is now commencing in a spirit of temperate optimism, but there is already sufficient evidence available as a result of the geological work to which I have alluded to justify a programme of test drilling on a not inconsiderable scale.

To sum up:—in certain areas there exist definite structures containing rocks which, outcropping at some distance away, show marked evidences of oil saturation. There appears to be good reason to presume adequate cover and adequate closure. There are still, of course, a number of speculative elements which can only be eliminated by the diagnosis of the drill, and only the drill can determine whether the rocks which exude oil at the outcrops do, in fact, contain oil in commercial quantities where they lie buried under adequate structural conditions.

It is unnecessary to emphasize the importance of the present activities in this country. To the geologists they are of absorbing interest; and the petroleum industry as a whole will eagerly await the decision whether or not Great Britain is to be added to the oil countries of the world, even though there seems little likelihood that, at the best, its potentialities will prove to be at all comparable with those of the major producers.

It is perhaps worth mentioning that interest and encouragement are not solely confined to petroleum operators; in general, all persons or bodies with whom negotiations have been conducted for land or facilities, recognizing the national importance of the work in hand, have adopted a reasonable and co-operative attitude.

As I have stated, no one can forecast the result of the search, but few events would be more satisfactory to the people as a whole than the discovery that there is oil in Great Britain, and I think that the

Council for the Preservation of Rural England are fully aware that we appreciate the necessity of preserving the beauties and amenities of the English countryside.

Petroleum Engineering.

In matters of petroleum engineering—as, indeed, in all branches of petroleum science—my difficulty lies in the selection of matter for comment. The difficulty arises from excess, rather than paucity of material.

Petroleum engineers throughout the world would be happier men if it could now be forecast that universal unit operation was a probability of the near future. The benefits of that system need no emphasis; and, wherever the system is practicable, there it is practised. The barriers to its world-wide adoption, as you are aware, are legislative, economic and, in a large measure, psychological. Too often, the individual refuses to forgo an immediate personal gain for the certainty of a widespread general benefit in which he would share to the extent of his just proportion, and no more. Let us hope that in some future Presidential Address an optimistic view will safely be taken of the prospects of universal unit operation of oil-fields. When that time arrives, we shall be nearer to the ideal of avoidance of waste—an ideal which is already eagerly pursued in most of our operations.

Although optimistic prophecy on the large-scale aspects of petroleum engineering may be denied to us, there are many respects in which satisfactory progress is already recorded and further development may be expected.

The search for oil at increasing depths has emphasized the need for all-round improvements both in equipment and technique.

The long strings of casing now being used call for steel capable of withstanding greater tensile and compression loads to meet the severe conditions to which the casing is subjected. Compression figures of casing are being raised by the introduction of a new process whereby the casing is manufactured in the normal manner, but with a larger outside diameter and a wall thickness slightly less than is required in the finished product. The casing is then compressed in special dies to the finished size. By this process the resistance to collapse value can be raised in the case of 6-inch casing from 5450 to 9150 lb. per square inch, an increase of approximately 68 per cent.

The corrosive action of H_2S and brine on drilling equipment and casing calls for more research work on this subject; acid-resisting steels are obtainable, but casing made from a suitable material costs approximately 2½ times that of normal Grade D. casing. Although,

where serious corrosion takes place in high-pressure wells, this high price may be justified as an insurance against costly repairs or even dangerous "blow-outs," its use would undoubtedly increase with a reduction in cost.

With the increasing use of internal-combustion engines for drilling purposes the need for more flexibility between the prime mover and the draw-works and slush pumps is being met by the introduction of hydraulic couplings. These couplings provide torque characteristics unobtainable with a direct drive and, although still lacking the flexibility of a steam engine, their use will obviate many of the objections associated with internal-combustion engine drives.

The need for pressure drilling as a means of combating the high pressures encountered in new fields is gradually being recognized. Its use is also being extended to other spheres of operations. In drilling through heaving shales this system, when used in conjunction with special muds, has proved of great assistance. Although introduced primarily as a means of drilling against high pressures, the system, using gasified oil as a flushing medium, is now extensively used for "drilling-in" wells of very low pressure in which the static head of normal drilling flush would hold back the oil shows, and possibly result in their being passed unnoticed.

The abnormal working pressures demanded of slush pumps used in high-pressure drilling may call for drastic changes in pump design. There is a tendency to revert to ram pumps with outside packed plungers as a means of overcoming the excessive wear which takes place in the pistons and liners of the present form of slush pump.

In view of the low efficiency and high steam consumption of the direct-acting steam pump, future practice may follow along the lines of power pumps operated by steam or internal-combustion engines either direct coupled or through tex rope, chain or hydraulic coupling drives.

Directional drilling will undoubtedly figure very prominently in the future development of oil-bearing horizons beneath the sea-shore, lakes, city areas, etc., where surface conditions prohibit the use of normal vertical drilling. The technique of directional drilling is making rapid strides both as regards the equipment employed and the number of operators who are being trained to carry out the work. Contrary to the general opinion that wells drilled off the vertical would result in serious difficulties from a production point of view, it has been found that, provided the inclination of a well is constant and in one general direction, sucker rod failures are not higher than in many of the old wells which, although more or less vertical, were by no means straight.

In the aggregate these brief references show that the practice of

drilling, although it continues to follow traditional lines, is constantly under examination in the light of working conditions and is subject to continual improvement.

Refining.

The necessity for the production of ever higher octane ratings is one of the outstanding features in the modern production of motor spirit.

Cracking temperatures have risen, with, of course, an increase in the amount of gas produced. During the last few years, intensive research on the polymerization of the olefinic content of cracked gas has been in progress, and it is more than probable that in all refineries of the near future plant will be installed for the production of polymer gasolines for use as motor fuel. These gasolines have an octane number of approximately 80, and possess good blending value.

Still more intensive is the research for high-octane aviation fuel, and a by-product of olefine production has been successfully converted into *iso*-octane with a rating of 100. The significance of this achievement lies in the fact that by increasing the rating from 85 to 100 a further 25 per cent. thermal efficiency becomes available.

It is not, I think, an exaggeration to say that for many years the primary object of virtually all refineries has been the production in the largest possible quantities of the highest-quality motor spirits. Neither is it an impossible exaggeration to think that a time may emerge when the development of the compression-ignition engine will render it desirable to convert a future excess of spirit into fuel for that type of engine. To do so would be a remarkable reversal of current procedure. To-day, it is common practice to crack gas oil for the production of spirit. 1½ gallons of gas oil yield approximately 1 gallon of spirit. On that gallon, a petrol-engined vehicle would travel, say, 15–25 miles; but on the 1½ gallons of gas oil a compression-engined car would do as much as 40 miles. The figures are stimulating to thoughts of future trends.

The compression-ignition engine, however, merits a section to itself.

Compression-Ignition Engines.

Marine. The gross tonnage of motor-ships is now approaching 12 million tons, and there is every prospect that it will increase with some rapidity.

The power of individual marine engines is also rising and, last year, units developing as much as 13,500 b.h.p. were constructed.

The consequences of these tendencies is that the consumption of fuel for marine purposes is being gradually diverted from furnace fuel to

diesel fuel. A commendable line of development would be the manufacture of engines capable of using the heavier grades now allocated to furnace purposes. It cannot be said, however, that there is any evidence that engine design is proceeding in this direction. Airless injection and higher revolution speeds both tend to make engines more fuel sensitive—and both are typical features of modern practice. Design, indeed, is taking advantage of improvements in the quality of diesel fuel in the same manner that petrol engine design benefited by improvements in the quality of petrol.

Road Vehicles. The compression-ignition engine is now firmly established for use in practically all motor buses and the heavier types of commercial vehicle. In fact, many manufacturers of this type of vehicle have practically ceased to incorporate petrol-fuelled engines. There is, however, a limitation in the sizes of compression-ignition engines which are likely to prove economic. The smaller the size of the engine and the higher the speed, the greater becomes the difficulty in obtaining good combustion. Moreover, the fuel pump and fuel injector equipment raise unduly the price of the small compression-ignition engine above that of a petrol engine of a similar size. It is doubtful, therefore, if the compression-ignition engine will make much progress for use in the normal private car. For the purposes of this type of vehicle a high performance is demanded, and the better power-weight ratio of the petrol engine gives it an outstanding advantage. In addition, the mileage run and quantity of fuel consumed are insufficient, normally, to enable the fuel economy of the compression-ignition type to counterbalance its greater capital cost.

A high standard of fuel quality is demanded for the high-speed compression-ignition engine. Just as octane rating is applied to motor spirit, so also a standard of ignition quality is essential for the fuel for high-speed compression-ignition engines. Suitable tests and acceptable standards are still more or less undecided, and work is being carried out in the laboratories of most countries on the problem.

Rail Transport. Locomotives and rail-cars are providing a very important means of utilizing compression-ignition engines, and it is probable that in the course of the next few years there will be much progress in this field. It has been found that the diesel locomotive may have an annual working time twice as great as that of a steam locomotive. Moreover, the fuel consumption of the diesel type ranges between one-sixth and one-tenth of that of the coal-fired locomotive.

Future development will depend largely on the evolution of an efficient and inexpensive form of transmission between the engine unit and the driving-wheels. At present, the larger locomotives are fitted with electric transmission; and in smaller engines, such as those of the

shunting type, some form of gear transmission is employed. The tendency is to extend the use of gearing with the addition of hydraulic coupling, thereby eliminating the more expensive electric equipment.

The impression formed by a general review of tendencies in the scientific activities of the petroleum industry is that we may expect an unhalting progress towards greater exactitude and enhanced efficiency. Geophysicists and geologists are testing new methods and fresh theories. Each test adds to the sum of their knowledge and experience. The technique of petroleum engineering is rendering possible the exploration and exploitation of ever greater depths below the earth's surface, with a high measure of safety and control. Unit operation, where it can be practised, gives greater knowledge of reservoir conditions, and leads to higher proportionate recovery of oil, conservation of gas, and greatly diminished costs. In the treatment of crude oil the efforts of chemists, physicists, refiners, and metallurgists are combining to convert crude, with a minimum of loss, into products of whatever specifications may be demanded by technical advances in the spheres of petroleum utilization.

The progress already attained is cause for satisfaction—not for the satisfaction which breeds contentment with things as they are, but for that which serves as a stimulus to further endeavour.

The affairs of the petroleum industry, although they are the primary concern of members of this Institution, are a part only of the wider affairs of our national fuel industries.

For many years I have adverted frequently in my public remarks to two themes: that the competition between oil and coal has operated far less disadvantageously to the latter than is popularly supposed; and that the time is long past, if it ever existed, when the coal industry should restrict its operations solely to the production of raw coal.

As to the first of these themes, the recent publication by the Fuel Research Board of an estimate of the quantities of coal saved by various forms of fuel economy has, I think, contributed largely to the enlightenment of the public mind, and shown that the falling coal consumption is not due to the competition of oil. Moreover, there is a widening realization that the products of oil cannot be consumed without manufacturing and other operations which make considerable demands upon coal. I hope that we may hear less in future of the so-called enmity between coal and oil; and that an atmosphere will be created in which friendly co-operation will thrive to the good of all.

The problem involved in the second theme—the limited activities of the coal industry—is less near to a solution. If the petroleum industry had been established upon the basis of the example set by

coal, we should to-day have had a number of groups of undertakings each concerning itself exclusively with a single type of operation. One group, for example, would seek for fields and produce crude oil. Another would be engaged in transport. A third would treat and refine; and so on.

Such a condition of affairs does, to some extent, subsist in the United States; but, fortunately, the common structure of the industry is more closely knit, with the result that any one group normally conducts and controls all operations from prospecting to ultimate sale.

The benefits of this type of organization are evident; and there will be more ground for optimism for the future of the coal industry when it shows signs of departing from its traditional structure and adopting some other which will enable it to produce and sell, not lumps of coal, but calories in the forms most acceptable to consumers. If such a structure had been adopted during the nineteenth century, the coal industry would now be a true fuel industry, producing coal, manufacturing gas and the by-products of carbonization, generating electricity and selling coke. Fuel economy, which is to-day a burden upon the industry, would be a source of added gain. Cheapness, which now connotes lower returns and distress among workers, would have brought compensations in increased demand.

It is not, I think, too much to hope that future progress will be shaped in such a mould. The Coal Mines Act of 1930, if it were aided by a co-operative spirit, would form an admirable basis for a new structure. The unification of coal royalties would be another support. Further aids, legislative and economic, could doubtless be provided.

Thus stimulated, a homogeneous coal industry would develop our great reserves of fuel to the national advantage and to its own benefit. Before long, I hope that we shall see not only a unification of royalties, but also a good measure of unification of the entire industry, with the production of coal, gas, electricity, coke or other products regulated to the exigencies of demand and controlled by the dictates of economics.

WELDING HARD-FACINGS ON DRILLING TOOLS.*

By J. Cuthill (Associate Member).

This paper was intended to deal with general field practice in welding, but as that subject would cover nearly the whole gamut of welding practice, and could hardly be dealt with in the scope of this paper, and as certain applications of welding are being dealt with by other authors at this Meeting, it is proposed to confine the remarks to one or two problems in connection with the application of hard-facing materials on which there have been some differences of opinion.

Before commencing that special subject, however, it is only right to say that welding practice generally has undergone intense development during the last few years, and an immense amount of technical and informative data is now available. In particular, attention is directed to the two volumes of the symposium on the Welding of Iron and Steel published by the Iron and Steel Institute in 1935. Unfortunately, the practice of welding does not seem to have received the same attention in this country, as the technical side and really good welders are difficult to find. Welding is a craft which seems to be easily acquired by some workers, but which cannot be trusted in the hands of many who have had much experience. It has been said that welding is an art, and that artists are born—not made.

It is greatly to the credit of oil-field technical staffs that so much has been done by them in the application of welding processes under difficult conditions, and with plant which is not always of the best type and most suited to the purpose. The necessity of training native labour, the remoteness from supply of raw materials and the urgency of repair work on a very miscellaneous class of machinery are difficult conditions which have brought out much ingenuity and which have forced oil-field welders into the forefront of actual practice. The repair of broken parts, the rebuilding of worn parts, the fabricating of new structures and tools for emergency use, the repair of boilers and high-pressure vessels are all sections of welding practice carried out regularly and efficiently by the welding departments in these remote areas, but as this class of welding can be called general engineering practice, and is efficiently dealt with in other literature, the present paper will be confined to the application of hard-facing materials.

The development of hard-facing materials for resistance to abrasion during the last ten years or so has been brought about almost entirely by oil-field demands. The uses and advantages of these materials have only comparatively slowly been recognized by other industries. It was found originally that "Stellite" applied to the cutting edges of the tools used in the drilling of oil wells greatly prolonged the life of the tools, and although the application of hard-facing to cable tools is necessarily limited by

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* Paper presented for discussion at the One Hundred and Sixty-ninth Meeting of the Institution of Petroleum Technologists, February 11th, 1936.

physical considerations, there is no doubt that its application to rotary tools has meant enormous economies in the way of saving in drilling time and cost of tools.

Since the recognition of the advantages which could be obtained, a great many hard-facing materials have been put on the market under a variety of trade names. The principal classes are as follows :—

1. Hard metal alloys consisting principally of combinations of some or all of the following :—

Carbon,
Chromium,
Tungsten,
Molybdenum,
Tantalum,
Cobalt, and sometimes,
Iron.

These alloys are made up in the form of rods which can be fused to steel, preferably by the oxy-acetylene process but also by the electric process.

Examples of this class are " Stellite " and " Stoodite."

2. Diamond substitutes, consisting principally of tungsten carbide, which has been fused and cast into various forms which will act like diamonds in cutting rock. These forms may be small slabs, cylinders and other shapes, but principally of granules of various sizes up to the size of a large pea. They are intended to be embedded in the cutting edges of the earth boring tools by fusing the steel of the tool or welding on with steel. They are not intended to be fused themselves, and cannot be fused by the oxy-acetylene flame, and are preferably applied by the oxy-acetylene process.

Examples of this class are " Borium " and " Haystellite."

3. Granular diamond substitutes, consisting principally of particles of tungsten carbide held in tubes of steel which can be conveniently welded to steel tools, preferably by the oxy-acetylene process, the steel tube on melting combining with the steel of the tool to hold the granules in place. In some cases the granular particles are cintered or fused together into welding rods with some binder, such as cobalt.

Examples of this class are " Tube Borium " and " Borod."

4. Tungsten carbide, in the form of granular powder which can be fused and welded to steel by means of the electric carbon arc. The deposit can be nearly diamond hard, but its hardness depends on the freedom of the deposit from the steels to which it is fused and on the carbon retained in the deposit after fusion.

Examples of this class are " Blackor " and " Britor."

A fifth class might be made of tungsten carbide in cintered blocks such as are used for machining tools, but as this class is inherently weak for the purpose under discussion, owing to the fact that its entire strength depends on the binder used, and is also costly, it has been employed to only a very limited extent for this purpose.

There is one particular difference between these various classes of hard-

facing to which attention should be directed. Classes 1 and 4 are essentially cakes, coatings, or scales of extremely hard material welded by fusion to the comparatively soft steel of the tools, whereas classes 2 and 3 comprise almost diamond hard particles, granules, or small pieces held in a matrix of steel, the matrix being welded by fusion to the steel of the tools. This difference has a very particular bearing on the question of the advisability of subjecting drilling tools to heat treatment after hard-facing.

Some operators, not content with applying the hard-facings, consider that they can improve matters by heating and quenching the drilling tools after the application of the hard-facing, and it is just possible that at times, and especially in the case of classes 2 and 3, they can show good results by this practice. Some manufacturers of hard-facing suggest that subsequent heat-treatment can be done, and there seems to be considerable difference of opinion on the subject.

It should be pointed out that any attempt at heating and quenching in the case of classes 1 and 4 is decidedly bad practice. It should be recognized that in these classes the hard-facing is in the form of a diamond hard, but

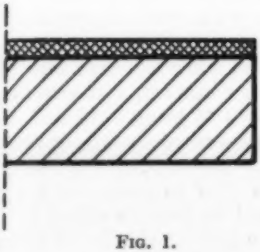

FIG. 1.

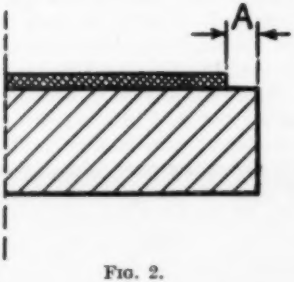

FIG. 2.

comparatively brittle, skin welded to a comparatively strong and tough body of steel. The coefficient of expansion of these hard-facings does not differ greatly from that of steel, and consequently little damage would be done if very slow heating and cooling took place, but the specific heat of the materials differs greatly from that of steel, and consequently any quick change in temperature such as occurs in too rapid application of heat, and especially in quenching, will mean that the change in temperature more rapidly affects the hard-facing than the steel and cracking is bound to result.

Fig. 1 represents in section a skin of hard-facing of classes 1 or 4 welded by fusion to the steel blade of a drilling tool. The hard-facing has a specific heat of, say, 0·065, as compared with the 0·117 of the steel.

If such a tool is heated slowly to a cherry red, the hard-facing and the steel will expand to practically the same extent, but if it is quenched, the instantaneous effect will be that the thin skin of hard-facing, owing to its surface exposure and lower specific heat, will tend to shrink to an extent diagrammatically represented as "A" in Fig. 2. The hard-facing, however, has no elasticity, and cracking is bound to result. Sometimes the hard-facing will flake off. Sometimes the cracks are easily detected; and sometimes the cracks are unnoticed, for the reason that they tend to close

up again, as the body of the steel contracts at a later stage than the hard-facing, but, nevertheless, they are there, and can be easily found under the microscope. Fig. 3 is a microscopic section showing the hard-facing applied to fish-tail bit steel. It will be noticed that the crack extends right to the surface of the steel, and that the hard-facing has broken or slipped away from the steel. It is quite conceivable that at times the cracks do not remain entirely in the hard-facing, but extend into the surface of the steel. A number of experiments have been made with a view to finding such extension cracks, but so far without success. Nevertheless, it is the author's opinion that they do exist, and it is suggested that the existence of such cracks is a contributory cause of breaking off of corners of drilling tools, which so frequently happens in the vicinity of hard-facing.

The quenching of tools faced with the classes of hard-facing listed as 2 and 3 may be attempted with much greater safety, for the reason that the matrix which holds the diamond substitute particles is steel or some substitute having a similar coefficient of expansion and specific heat and similar toughness to the steel of the tool, so that it is unlikely to crack. Nevertheless, the sudden quenching, especially if water quenching is attempted, is likely to crack the diamond substitutes, and in any case it must be emphasized that there is no real necessity for attempting to harden the steel to which hard-facing is applied.

Before the advent of hard-facings, fish-tail and other bits were generally made from steel of about 0·5 per cent. carbon or upward, and sometimes with admixtures of alloys. This steel permitted of being hardened to a safe extent by quenching. Since hard-facings came into vogue, however, the high carbon percentage was not considered necessary, and it has been reduced to 0·4 per cent. or even less, with a view to providing a safer material to which welding can be applied, and to provide a less brittle support for the hard-facing. Any attempt to harden this lower carbon steel with a view to providing better cutting qualities in the steel itself, will have very little, if any, effect, and any attempt to do so with a view to providing a better support for the hard-facing will be a mistake; in fact, it may have the opposite effect, in making the steel too brittle. Any attempt at hardening the hard-facings by heat-treatment will be of no avail. They cannot be made harder than in the "as welded" condition.

The steel of the tool should be considered as a holder for the hard-facing which is the real cutting tool. All that is necessary is to provide in the steel a sufficiently strong and homogeneously tough support to which the hard-facing can be effectively welded.

Normalizing is a different matter, and many operators do this as a regular practice for a very good reason. It will be recognized that the welding of hard-facings to bulky articles of high carbon steel is likely to leave local strains in the metal owing to the concentration of heat at any one place as the welding proceeds. These strains are liable to be very severe, and can exceed the rupture point of the material. They can be dangerous when there are quick changes of section, and can be accentuated when there are inherent impurities in the steel, or when the steel has been burned during welding or previous heat-treatments.

Normalizing consists of heating the tool, or as much of it as is necessary, slowly and evenly to the correct temperature (usually about 1550° F.),

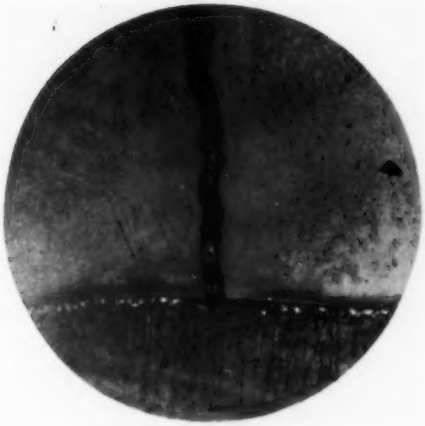

FIG. 3.

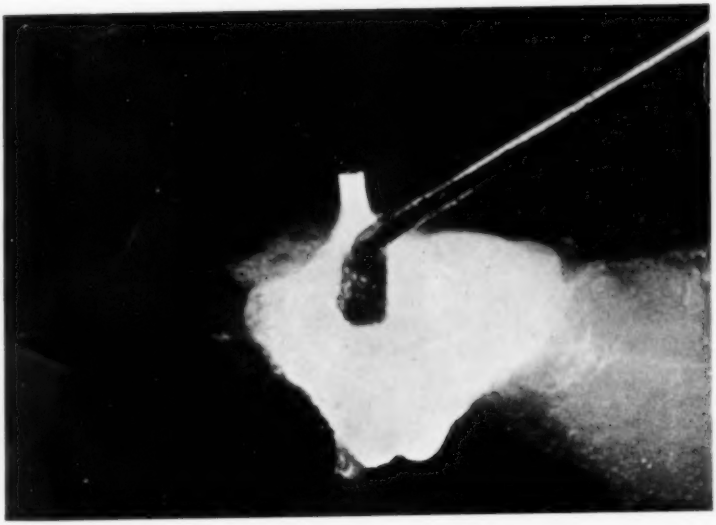

FIG. 4.

[*To face p.* 208.

Fig. 5.

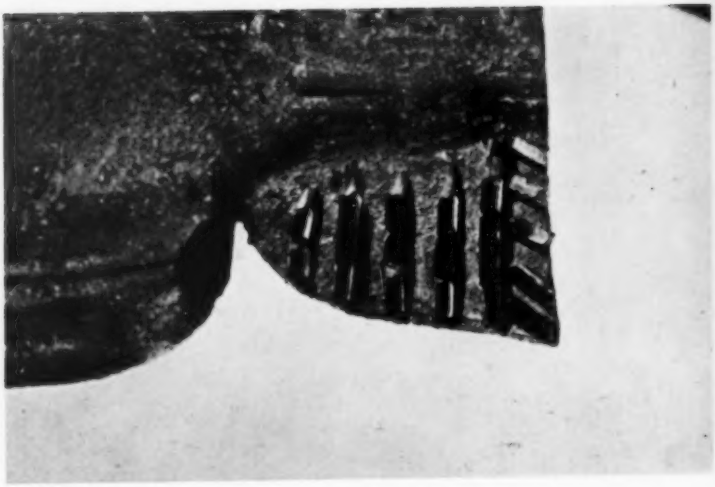

Fig. 6.

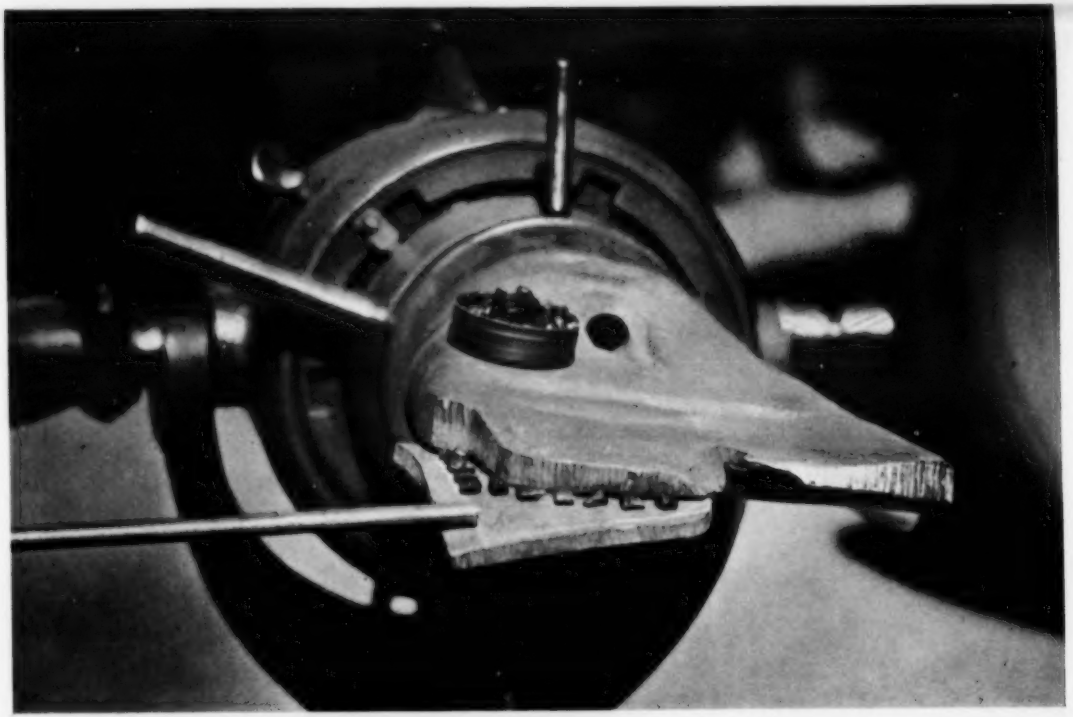

FIG. 7.

g at that temperature for a sufficient soaking time dependent on the ss of the metal, and allowing to cool in air free from draught.

alizing can be carried out with perfect safety in the case of tools) w. . classes 2 and 3 of the hard-facings have been applied, but greater are should be taken in the case of the other classes.

To summarize the above :—

1. It is not necessary or advisable to attempt to harden tools which ve been hard-faced, and quenching in water should never be attempted.
2. Normalizing is advantageous and advisable, but should be carried out with care and under proper supervision.

A brief description of one or two of the most modern methods of applying hard-facing in oil-field practice will now be given.

The drilling tool, if not new, should have the old hard-facing removed, and it should then be dressed by forging to the shape required. The portion of the cutting edges which are to be hard-faced should then be cleaned free from scale, etc., by grinding. The tools should then be placed in a holder or on a table in a convenient position, in such a manner that the surface to be welded is held horizontally.

First Method.—The diamond substitutes are placed in a convenient position, and an oxy-acetylene welding torch is adjusted to have a slightly reducing flame. This flame is played over the substitutes and the edge of the bit to be welded, to raise the temperature and avoid the excessive ... ie t. sudden application of welding heat to cold metal. The flame is then concentrated on a spot at the edge of the tool until the surface of the steel becomes molten, and at the same time the end of a welding rod of medium carbon steel is heated to the melting point. The rod is then touched to a piece of substitute, and the flame is played on it for an instant to make it adhere so that it can be lifted by the rod and placed in the required p ion in the hot spot at the edge of the tool (Fig. 4). Further application of . orch will ensure . ostitute being well embedded in the steel of the tool, and it should . covered with steel melted from the welding rod. Additional pieces . mond substitute are applied in the same manner to the cutting an . aming edges of the tool at intervals of about ½ to 1 inch apart, and additional rows are added behind the first row to provide additional cutting teeth when the first row has worn off.

A tool dressed in this manner would quickly wear away between the pieces of substitute, leaving them on the ends of claw-like projections which might break off. It is advisable, therefore, to overlay the whole surface which has had the substitutes applied with a coating of fine granular diam . subs ute which is made up in steel tubes (class 3). Sometimes two or . coatings of this material can be applied with advantage. The coating will then appear as in Fig. 5. It is usual to use forms of thick copper plate which can be applied to the edges of the tool in the nature of a mould to limit the flow of the hard-facing material, and so obviate the necessity of much subsequent grinding to bring the tool to the size required. This grinding is costly both in waste of hard-facing and in grinding wheels.

Second Method.—Many operators have found that a better cutting effect can be obtained by embedding the diamond inserts in grooves cut in the cutting and reaming edges of the tool, as shown in Fig. 6. These grooves

are sometimes cut by the oxy-acetylene flame, but this is bad practice, owing to the notching, and consequent weakening effect on the steel of the tool, and to the fact that a coating of oxide is left on the steel. It is much better to cut the grooves by means of a small hand-grinding wheel. The diamond substitutes are then laid in the grooves as shown, and by means of the torch and medium carbon steel welding rod embedded in place and well covered with steel, after which the surface should be well covered with the fine granular material embedded in steel as in the first method described.

Third Method.—A method which has been found very effective is to cut grooves as above and fill them with the fine granular tube-filled material and cover with medium carbon steel, after which one or more coatings of the tube material can be applied to the surface.

Fourth Method.—Tungsten carbide can be applied to the cutting surface by using one of the proprietary makes of tungsten carbide powder (class 4). This powder is spread to a thickness of about $\frac{1}{4}$ inch over the surface to be covered. Using a carbon as a positive electrode, an arc is struck at the edge of the area, and the powder is then melted and fused to the steel. A thin coating about $\frac{1}{16}$ inch thick of tungsten carbide fused to steel is produced. A second and third application is made in the same way, the upper layer being almost pure tungsten carbide of almost diamond hardness.

Fifth Method.—Some operators, instead of re-dressing a tool to the proper shape by forging, cut away the worn edge by means of the acetylene flame, as shown in Fig. 7. A copper plate form is then held in position on the cutting surface, which is held downwards. Rows of substitutes are placed in position on the copper plate, and by means of a medium carbon steel rod and electric arc the whole cutting edge is rebuilt on top of the substitutes, as shown in process in Fig. 8. On completion, the bit is turned over, and the cutting surface is cleaned and covered with the granular tube material. This may seem a somewhat risky process, owing to the fact that the block of steel forming the cutting edge can only be considered as cast metal. Nevertheless, in the hands of competent operators it has proved quite effective, and has the advantage of prolonging the life of the bit.

There are variations in these methods recommended by each maker of the hard-facing materials, but they will serve to indicate generally how the hard-facings are applied. An important point is to see that the hard-facing is amply supported by the steel of the bit. It is a common fault to draw out the steel edge of the bit to an almost feather edge. The application of hard-facing to such an edge is of little use. The steel is very apt to be burned during welding, and is likely to break away rapidly.

The author wishes to express his thanks to the Stoody Company for the use of some of the illustrations.

THE WELDING OF PRESSURE VESSELS.*

By S. F. Dorey, D.Sc., M.Inst.C.E.†

During the past two or three years such progress has been made in autogenous welding processes and apparatus that the Committee of Lloyd's Register of Shipping has deemed it not only prudent but necessary to make provision in the Rules for the acceptance of fusion-welded pressure vessels.

In 1934 the Society's Rules for boilers and unfired pressure vessels such as air receivers were revised, and it is to be noted that fusion welding by the electric arc or oxy-acetylene-gas process is now no longer prohibited for plates in tension. Although no published Rules have been issued governing the welded construction of pressure vessels intended for marine purposes, such Rules will be promulgated in due course; in the meantime, the Committee is in a position to give proposals very careful and authoritative consideration and to treat each individual case on its merits.

The Society's activities in connexion with non-marine work have increased considerably during the last year or so, and it has been found necessary to legislate for the welding of pressure vessels intended for land purposes. Accordingly, in July 1934, the Society published "Tentative Requirements for Fusion Welded Pressure Vessels intended for Land Purposes," and since that date numerous welded pressure vessels, including boiler drums, steam containers, chemical reaction chambers, air receivers and refrigeration plant, have been constructed under survey. It is safe to say that without welding some of the latest advances in steam generating plant could never have been made. . . . As examples of this, mention might be made of the Loeffler and Sulzer high-pressure boilers, and the Velox Steam Generator, the main components of which involve a considerable amount of fusion welding.

The following remarks are mainly intended to direct attention to some of the important factors concerning the welding of pressure vessels.

The Parent Plate Material.

One of the first considerations in regard to the manufacture of fusion-welded boiler drums is the selection of the parent plate material. Emphasis has been frequently laid on the necessity for providing weld metal which after deposition will possess the same chemical and physical properties as the parent plate. At the same time, it is not always realized that the desired complete identity of parent plate with weld metal as deposited is quite impossible to obtain. The fact will always remain that weld metal is cast metal, whilst the parent plate is wrought. There is thus a fundamental difference in metallurgical condition, apart from chemical composition, which can be modified only by subsequent heat treatment.

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* Paper presented for discussion at the One Hundred and Sixty-ninth Meeting of the Institution of Petroleum Technologists, February 11th, 1936.

† Chief Engineer Surveyor, Lloyd's Register of Shipping.

There are three main factors to bear in mind:

1. The effect of differential freezing during welding.
2. The possibility of electrolytic action in service.
3. The strength properties of the joint.

It is not difficult to understand that when molten weld metal is run between the solid surfaces of two adjoining steel plates, these surfaces are themselves reduced to a molten condition, and an intimate mixing of the two fluids takes place. The fusion zone of a welded joint consists, therefore, of a diffusion of constituents of the parent metal into the weld, and vice versa. It is for this reason that special consideration must be given to the chemical composition of steel plates intended for welding.

Carbon is the most important strength-giving constituent in steel, and experience indicates that up to 0·4 per cent. carbon content there is no special difficulty in effecting a satisfactory ductile weld. Boiler quality mild-steel plate may contain between 0·1 per cent. and 0·2 per cent. carbon, depending upon the tensile strength required. Arc welding has a decarburizing effect on the plate immediately adjacent to the weld, and it is possible, therefore, to cause a slight reduction in tensile strength in this position. Certain elements such as manganese and silicon may be introduced through the medium of the electrode and serve to prevent excessive decarburization.

Both manganese and silicon are powerful de-oxidizing agents, and when contained in the electrode they are substantially reduced in quantity during the process of deposition. Manganese has a toughening effect on mild steel, and is generally present in proportions up to about 1·0 per cent. In considering the favourable effect of manganese in steel, it must be remembered that a slight increase above a content of 1·0 per cent. may render the steel prone to hardening as the result of the heat effect during welding.

Opinions differ as regards the maximum silicon content suitable for steel intended for welding. A certain quantity of silicon is required in the electrode in order to prevent the absorption of gases in the steel which at high temperatures possesses great affinity for hydrogen, nitrogen, oxides of carbon, etc. If, however, the parent steel already possesses an appreciable silicon content, it appears possible that the molten mixture of parent steel and weld metal in the fusion zone may be unduly "killed" during cooling, and the resultant solid metal at the weld junction will be brittle and prone to cracking. In these circumstances, it is suggested that this may be the reason for some of the failures which have occurred in the fusion zone during welding. Consideration of the problem leads to the conclusion that it is desirable to keep the silicon content in the steel as low as possible.

It is unlikely that rolled-steel plates intended for welding will contain injurious quantities of phosphorus and sulphur. From the welding point of view it is, however, well to realize that the effect of phosphorus is to increase the sensitivity of steel to overheating, and to render the metal cold, short and brittle. Sulphur, on the other hand, renders the steel red short—that is to say, brittle when it is hot. So far as sulphur is concerned, the important consideration is not so much the quantity, but

rather the condition in which it is present in steel. These factors are well known to steel makers, and it is not intended to dwell upon them here.

It is of interest to note that the report of the Committee on Welding Containers set up by the Department of Scientific and Industrial Research states that the Committee came to the conclusion that the requirements for welding would be satisfied by a steel conforming to the following analysis:

Composition.

Carbon	0·1–0·2	per cent.
Sulphur	0·04 max.	,,
Phosphorus	0·05 max.	,,
Manganese	0·4–0·6	,,
Silicon	0·2 max.	,,

The balance being iron.

Tensile strength 24–28 tons per sq. inch.
Elongation 27 per cent. min. on 8 inches.

The Committee also makes the recommendation that the steel should be produced by the acid or basic open-hearth process.

It is true that this suggested specification is in respect of forge welding. For fusion welding it is considered that both the phosphorus and silicon should be reduced to proportions not exceeding 0·04 per cent. and 0·05 per cent. respectively.

It should be added that the ultimate quality of the welded joint is not only influenced by the chemical composition of the steel plates, but depends to some extent on the nature and amount of the work done on the ingot to produce the plate.

The Electrode.

Of equal importance to the selection of the parent plate material is the choice of welding rod or electrode which has to be melted down in order to provide the weld deposit.

It is now generally understood that bare wire electrodes are unsuitable for the welding of joints which require ductility, toughness and strength. This is mainly due to the complete absence of any protection of the molten weld metal from atmospheric contamination. What is not generally understood, however, is that the mere fact that an electrode is covered does not mean that the electrode is any more suitable for its purpose than bare wire. Those responsible for the details of welding specifications should note that it is not sufficient to specify that "covered electrodes should be used," but they should go further, and state that the nature of the covering should be such as to shield the arc stream and deposited weld metal from atmospheric contamination and to prevent oxidation of the weld. It does not follow that if the arc stream and deposited weld metal are shielded from atmospheric contamination, oxidization of the weld is automatically prevented, since some electrodes may have what is called an oxidizing coating—that is, a thick covering in which the concentration of oxygen may even be greater than could be obtained with bare wire electrodes.

These thick-coated or heavily fluxed electrodes include in the siliceous material of the covering considerable quantities of ferric oxide. The weight of the flux in these cases has the effect of ironing out the molten and plastic weld metal, so that the resultant finish of the weld is smooth

and clean. Such electrodes are specially suitable for producing a smooth, concave contour in fillet welds, but unfortunately the weld metal is highly oxidized, hard and lacking in ductility.

Obviously, such electrodes are quite unsuitable for the welding of pressure vessels, although they fully comply with the simple requirement that electrodes should be covered.

The electrode covering has other important functions besides the shielding of the arc from atmospheric contamination. In this connection, reference might be made to the importance of ferro-manganese, a de-oxidizing agent producing an exothermic reaction which has the effect of retarding the rate of cooling of the molten pool, thus giving the gases and inclusions time to escape before solidification of the weld metal commences. Such exothermic reactions increase the speed of welding because of the increased melting-off rate of the electrode, the welding heat being provided from two sources, viz. the electrical energy in the arc and the heat generated by chemical reaction.

It will be appreciated that for vertical and overhead welding a quick-freezing weld metal must be deposited. The practical considerations governing the making of welds in these positions preclude the use of heavily fluxed shielded arc electrodes. For these reasons the welding of important pressure vessels should always be done in the flat underhand horizontal position.

There need be no special difficulty in selecting an electrode suitable for the welding of these vessels, provided the essential requirements are understood and strictly enforced.

In regard to the selection of electrodes, the following requirements are suggested for consideration :—

1. *Type of Electrode.*—The electrode should be of the type which provides a reducing gas shield to the arc and a neutral slag over the deposited weld metal. It should be easy to manipulate, non-spluttering and capable of maintaining a steady arc and uniform melting rate. The slag should be easily removable from the surface of the weld metal after cooling.

2. *Chemical Analysis.*—It is thought that the electrode maker should be allowed a certain freedom in his choice of core wire for electrodes, and it does not seem to be in the interests of progress and development for the user to specify the exact chemical analysis of core wire and covering, or whether the core wire should be made from rimmed or silicon killed steel. It is, however, important that the desired chemical composition and mechanical properties of the weld metal, as deposited, should be clearly defined within reasonable limits.

Consideration of the analyses obtained from a number of high-quality weld deposits made in low carbon mild steel plates suggests that the following percentages for the various elements in weld metal might form a reasonable basis for comparison :—

Composition.

Carbon	0·06–0·12	per cent.
Silicon	0·05	,,
Manganese	0·4–0·5	,,
Phosphorus	0·015 max.	,,
Sulphur	0·015 max.	,,
Nitrogen	0·015 max.	,,

3. *Physical Properties of Weld Metal.*—The quality of the weld metal as deposited from the electrode may be assessed by preparing the following test specimens from a sample joint made between boiler quality mild steel plates 1 inch in thickness.

(*a*) All weld metal tensile specimen.
U.T.S. = 26–30 tons per sq. inch.
Elongation on 2 inches = 20 per cent.
Reduction of area at fracture = 35 per cent.

(*b*) Transverse reduced section tensile specimen taken across the joint.
U.T.S. = 26–30 tons per sq. inch.

(*c*) Bend Test Specimen.
Thickness = 1 inch.
Width at weld = 2 inches.
To be bent cold to an angle of 120°.

Specimens (*b*) and (*c*) should be formed in such a manner that the stress is concentrated at the weld. This may be effected by drilling the test plate as shown in Fig. 1.

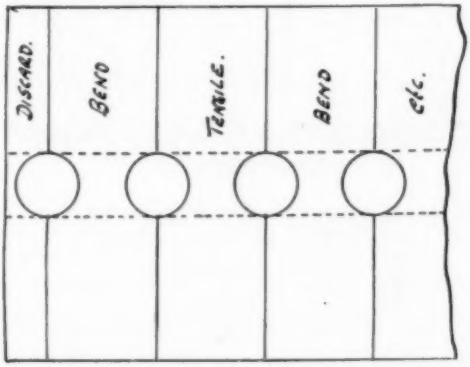


FIG. 1.
TEST PLATE FOR ELECTRODE SELECTION TESTS.

The transverse tensile specimen should be examined at the fracture. The surfaces of the fracture should reveal a sound, homogeneous weld, substantially free from coarse crystallinity, porosity and slag inclusions.

It is suggested that these simple tests, together with the chemical analysis of the weld metal, should be sufficient to indicate whether or not the electrodes are suitable for the welding of pressure vessels.

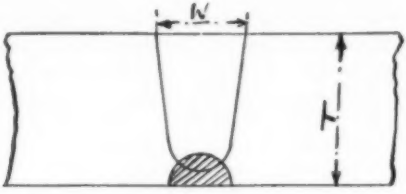
In cases where the routine testing of the pressure vessels involves X-ray examination, the sample test plates should always be X-rayed before preparing the specimens. The position from which each specimen is cut should be marked on the X-ray negative.

An important factor in the choice of an electrode is ease of manipulation, and here reliance should be placed on the opinion of an experienced and trustworthy welding operator.

It is, of course, impossible for many of those interested in the manufacture of welded products to make an exhaustive study of electrodes. There are many types available, good, bad and indifferent, and some are more suitable than others for work of special character. The best advice that can be given is to deal with reputable electrode makers only, and it will be found that most of them will frankly admit the limitations of their different electrodes.

As the result of the electrode selection test, the main factors in weld metal deposition should be established, and the desired current values, arc lengths and rate of deposition to give the best physical properties in the weld should be known.

It is, however, necessary to consider various aspects of welding technique as applied to pressure vessels, which have been found to influence the nature of the result obtained.



SHADED PORTION TO BE CUT OUT AND WELDED UP FROM UNDERSIDE.

T	3/4"	7/8"	1"	1 1/8"	1 1/4"	1 1/2"	1 3/4"	2"
W	5/8"	5/8"	3/4"	3/4"	7/8"	7/8"	29/32"	15/16"

FIG. 2.

TYPE OF JOINT FOR FUSION-WELDED BOILER DRUMS.

WELDING TECHNIQUE.

It is desired to stress the importance of accurate "fit up." The welding groove which forms the seam should be of the U form, as narrow as practicable and with the sides nearly parallel. Care should be taken to see that the butting edges are properly in line, and if there is any gap at all at the root of the joint, that it is consistent for the entire length of the seam. The plate edges to be welded should be machine cut, clean and free from the burrs sometimes caused during handling.

Certain electrodes deposit weld metal sufficiently ductile to allow the complete butting of the plate edges without any shrinkage gap.

A backing strip should be tack welded under the seam for the full length. The material and dimensions of this strip are unimportant, provided it is thick enough to withstand the impingement of the arc without burning.

The longitudinal joint should be tack welded at the root.

By means of jacks the circular shell should be forced into an elliptical

shape, the major axis being in line with the longitudinal joint. Struts should be inserted to hold the vessel in this shape until welding is complete.

The dimensions of the ellipse to which the cylindrical shell has been forced will largely depend on the diameter required for the finished drum and the thickness of the plate. It is not a difficult matter, and a good fitter will know by experience what allowance should be made. Generally the difference between the major and minor axes may be between 0·5 and 1 per cent. of the designed diameter of the drum.

On completion of the welding of the longitudinal seam, the struts and backing strip should be removed, and by means of a pneumatic chisel, a vee should be cut from the inside of the shell right along the seam. This

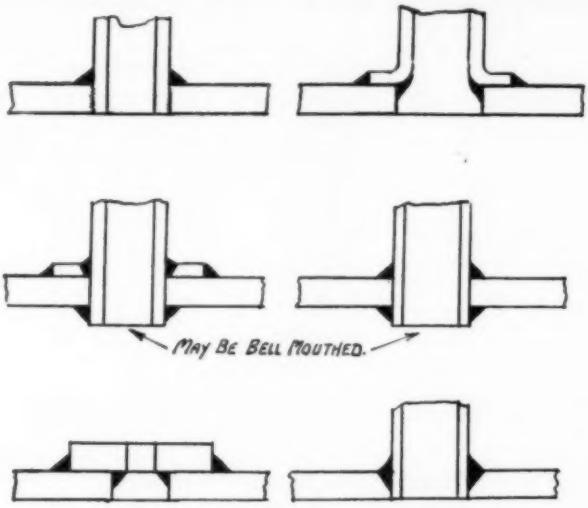


FIG. 3.

TYPICAL METHODS OF ATTACHING BRANCH CONNECTIONS TO PRESSURE VESSELS.

will cut out practically the whole of the first run of weld metal deposited in the joint.

It should be explained that this first run is contaminated from the underside, and usually contains trapped slag, cracks and blow-holes. It may be regarded as doubtful weld metal, and for important pressure vessels should be removed.

On both the inside and the outside the weld should be built up, *i.e.* reinforced, so as to ensure the refining of the crystal structure throughout the full depth of the weld. The reinforcement should subsequently (before X-ray examination) be removed by grinding the weld flush with the parent plate.

Before attaching the drum ends, the shell should be calibrated for circularity and, if necessary, re-rolled or re-formed to bring it within the tolerance allowed. This operation is seldom found necessary after a little experience has been obtained.

The form of the welding groove for the circumferential joints should be the same as for the longitudinal, and the plate edges should be prepared and butted with the same accuracy. The backing strip is usually tack-welded to the cylindrical shell and forms a ring over which the end plate can be slipped. The same procedure of welding and cutting should be carried out.

It is important to arrange that all the welding be done underhand—that is, with the electrode vertical and the weld groove horizontal. For this reason, arrangements must be made so that in welding the circumferential seams the drum can be rotated. On no account must the welder be allowed to continue his run of weld metal round the circumference to such an extent that the molten weld metal runs in front of the electrode.

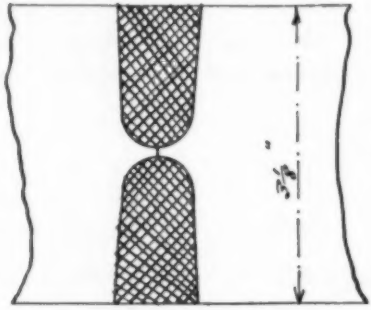


FIG. 4.

FORM OF JOINT USED BY MESSRS. JOHN THOMPSON (WOLVERHAMPTON), LTD., IN THE CONSTRUCTION OF THICK HIGH-PRESSURE AUTOCLAVES.

MANUAL AND MACHINE WELDING.

A problem which, sooner or later, faces all those concerned in the manufacture of fusion welded pressure vessels is that of deciding whether manual or machine welding is best for their purpose.

The use of a welding machine enables the employment of larger electrodes, higher welding currents and faster welding speeds. These are important advantages from the point of view of production. At the same time, it must be remembered that great accuracy must be maintained in the preparation and "fit up" of the vessel to be welded. In manual welding any slight inaccuracy in the joint can be observed by the welder, who can manipulate his electrode accordingly.

From the economic point of view, therefore, it is necessary, when taking account of the increased welding speed, to make due allowance for the time and care required in fitting up the vessel preparatory to welding.

Technical considerations indicate that machine welding of the longitudinal and circumferential seams possesses distinct advantages over manual welding. In the first place, it is possible to maintain a standard set of welding conditions under which the consistency of the weld deposit can be ensured throughout the full length of the seam, there is no undue fluctuation

of arc length, and further, the operation of the machine does not induce the same degree of tiredness in the welder.

There are a number of different types of fusion welding machines (*i.e.* automatic welding heads) available, but they are mainly used in conjunction with bare wire electrodes. The conditions required for the welding of important pressure vessels necessitates the design of welding heads specially for the purpose.

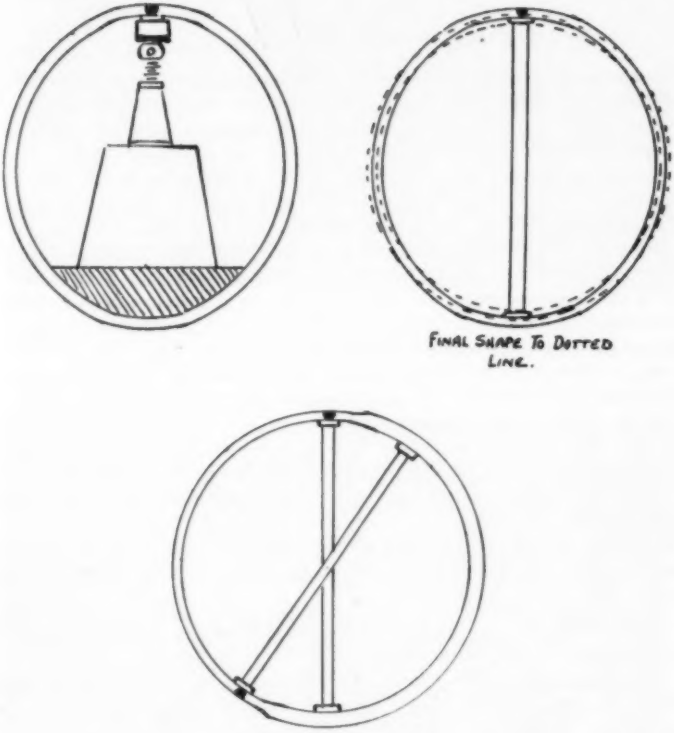


FIG. 5.

METHOD OF PREPARING BOILER DRUM SHELLS FOR WELDING.

The following points should be borne in mind when considering the application of machine welding to pressure vessels.

The groove should be of the U type, the width being slightly greater than the diameter of the electrode. The weld metal should be deposited in straight runs, one on top of the other. Although oscillating devices are sometimes incorporated in welding machines, their use is not always satisfactory, and is not recommended.

The drum shell before welding should be slightly elliptical, the difference between the major and minor axes being 0·5 to 1 per cent. of the designed

diameter of the drum. This can be effected by rolling the shell plate circular and then forcing it to the elliptical shape by means of inserting vertical struts directly under the longitudinal seam.

The preparation and procedure should be similar to those already described in dealing with the preparation of drum shells for welding. It should, however, be added that it is necessary to fix the drum in position under the welding head in such a manner that the seam is in direct line with the direction of travel of the head, and it should be ensured that the drum is level.

Residual Stress and Stress Relieving.

The problems relating to residual stress in weld metal continue to receive considerable thought and study. A variety of methods of investigation have been adopted by different research authorities in their attempts to evaluate the magnitude of residual stress and the nature of its distribution.

Residual stress may be defined as the stress which exists in weld metal as the result of differential cooling. The stress may be complex in character and of varying intensity across any one plane. It is caused by the shrinking of cooling weld metal, and is aggravated when the metal is deposited between restrained or partly restrained plates.

It is often erroneously inferred that severe distortion is indicative of serious residual stresses. On the contrary, it is in the absence of distortion that serious locked-up stresses are likely to occur. The "fit up" of any structure which is to be welded should, when possible, be such as to allow movement (*i.e.* distortion) to take place, so that the final shape of the distorted structure is the shape desired.

In the case of pressure vessels this principle is applied by commencing to weld with the vessel constrained to an elliptical shape; the result of the distortion due to weld metal shrinkage is that the final shape of the vessel is approximately circular.

In regard to the stress-relieving treatments which may be applied to pressure vessels, there appears to be three methods worthy of consideration, viz. :—

1. *Normalizing, i.e.* heating to above the upper critical temperature and cooling in a still atmosphere.
2. *Annealing, or Stress Relieving, i.e.* heating to a temperature slightly below the lower critical and cooling either in a still atmosphere or in the furnace.
3. *Stress Relieving by Means of Mechanical Straining.*

So far as alloy steel and weld metal are concerned, the special circumstances of individual cases must be considered on their own merits before arriving at any conclusion in regard to heat treatment, but there can be little doubt that for ordinary mild steel welds normalizing is desirable. In view, however, of the difficulties entailed in imposing such treatment on cylindrical pressure vessels and complex structures, inspecting authorities are bound to hesitate before including "normalizing" in their rules and specifications.

One of the main difficulties which has often been stressed in regard to the normalizing of cylindrical pressure vessels is the possibility of structural

FIG. 6.

WELDED CYLINDRICAL SHELL, 3½ IN. THICK, FOR HIGH-PRESSURE AUTOCLAVE. MADE BY MESSRS. JOHN THOMPSON (WOLVERHAMPTON), LTD.

FIG. 7.

DISHED END-PLATES FOR AUTOCLAVE SHOWN IN FIG. 6. EACH OF THESE WAS PRESSED IN A SINGLE OPERATION.

[*To face p* 220.

FIG. 8.

THE FINISHED AUTOCLAVE. INTERNAL DIAMETER, 6 FT.; LENGTH 11 FT. 8¼ IN.; SHELL PLATES AND DISHED ENDS, 3¼ IN. THICK. WORKING PRESSURE, 900 LB. PER SQ. IN. WORKING TEMPERATURE, 320° C. (608° F.).

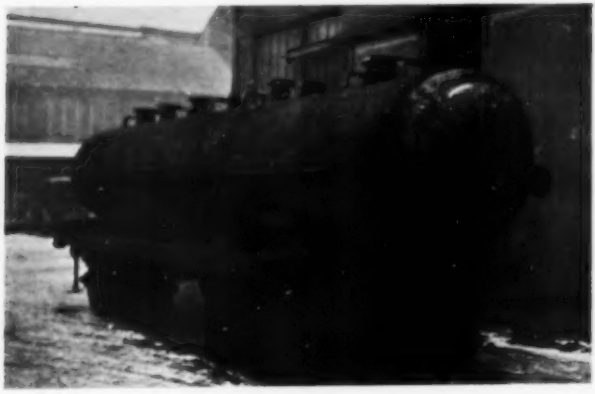


FIG. 9.

ALL-WELDED WATER-TUBE BOILER DRUM MADE BY MESSRS. JOHN THOMPSON (WOLVERHAMPTON), LTD., OVERALL LENGTH, 26 FT.; INTERNAL DIAMETER, 3 FT. 9 IN.; PLATE THICKNESS, $1\frac{5}{32}$ IN. WORKING PRESSURE, 315 LB. PER SQ. IN.

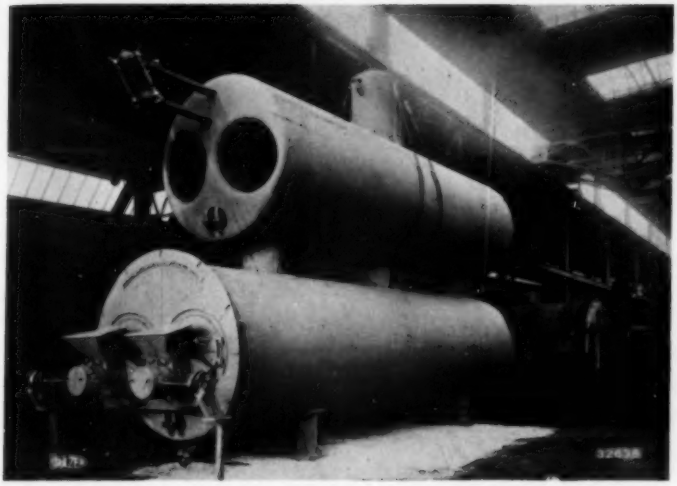


FIG. 10.

FUSION-WELDED DOUBLE LANCASHIRE BOILER MADE BY MESSRS. SULZER BROS., WINTERTHUR. WORKING PRESSURE, 270 LB. PER SQ. IN.

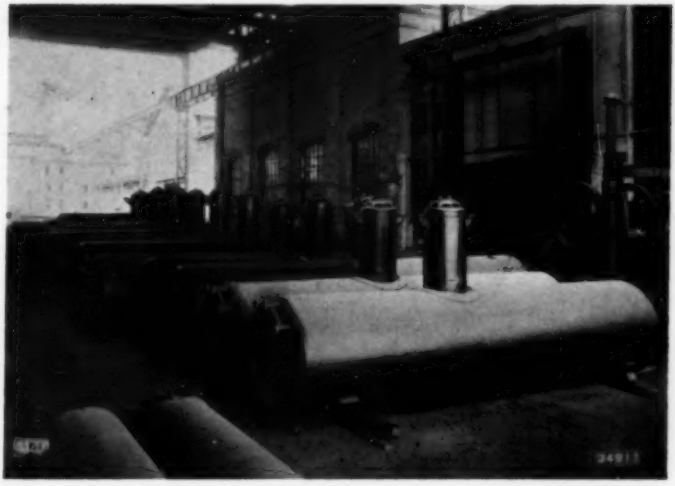


FIG. 11.

FUSION-WELDED CORNISH BOILERS MADE BY MESSRS. SULZER BROS.

FIG. 12.

FUSION-WELDED HEAT ACCUMULATORS.

FIG. 13.

FUSION-WELDED PRESSURE VESSEL MADE BY MESSRS. SULZER BROS., AFTER BEING SUBJECTED TO A BURSTING TEST. THE VESSEL HAD SPIRAL SEAMS AND RUPTURE TOOK PLACE AT 2300 LB. PER SQ. IN. THE WELDED JOINTS REMAINED INTACT, THE FRACTURES BEING CONFINED TO THE SOLID PLATE. LENGTH, 16 FT. 6 IN.; DIAMETER, 6 FT.; PLATE THICKNESS, $1\frac{7}{16}$ IN.

FIG. 14.

FUSION-WELDED OIL TANK MADE BY MESSRS. SULZER BROS. LENGTH, 52 FT. 6 IN.; DIAMETER, 6 FT. 6 IN.; PLATE THICKNESS, 0·35 IN. WORKING PRESSURE, 57 LB. PER SQ. IN. NOTE SPIRAL WELDED SEAMS.

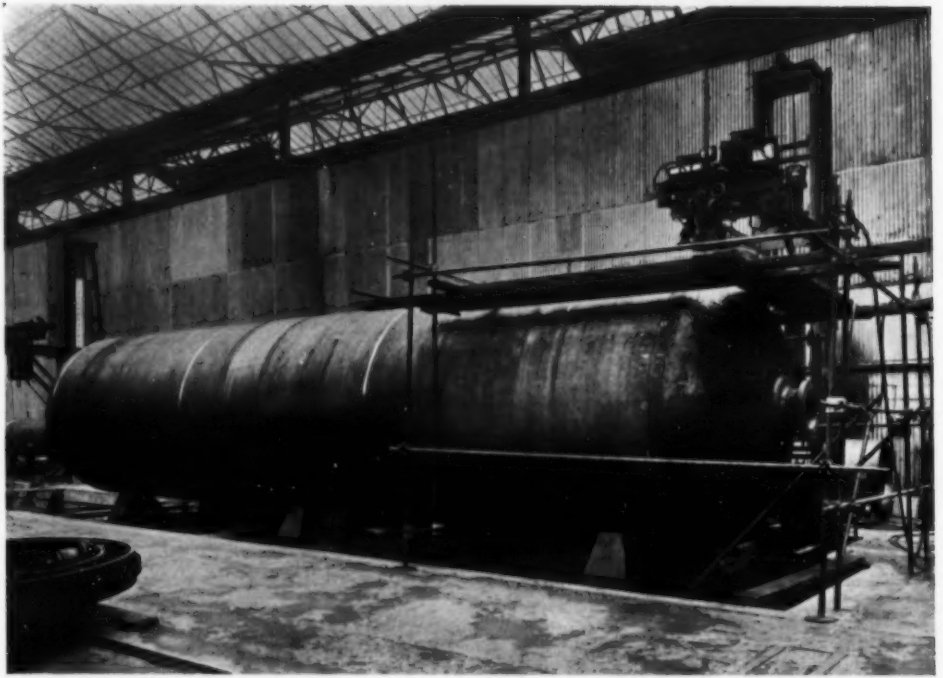


FIG. 15.

WELDED PROPANE STORAGE TANK MADE BY MESSRS. BABCOCK & WILCOX, LTD. INTERNAL DIAMETER, 10 FT.; LENGTH, 40 FT.; PLATE THICKNESS, $1\frac{5}{8}$ IN. WORKING PRESSURE, 250 LB. PER SQ. IN.

FIG. 16.

WELDED STABILIZER TOWER MADE BY MESSRS. BABCOCK & WILCOX, LTD. WORKING PRESSURE, 400 LB. PER SQ. IN.

FIG. 17.

ONE OF A NUMBER OF GAS-OIL SEPARATORS MADE BY MESSRS. BABCOCK & WILCOX, LTD. DIAMETER, 2 FT. 6 IN.; LENGTH, 10 FT.; PLATE THICKNESS, $1\frac{11}{16}$ IN. WORKING PRESSURE, 1000 LB. PER SQ. IN. THIS VESSEL IS PARTIALLY RIVETED AND PARTIALLY WELDED.

WELDED PROPANE STORAGE TANK MADE BY MESSRS. BABCOCK & WILCOX, LTD. INTERNAL DIAMETER, 10 FT.; LENGTH, 40 FT.; PLATE THICKNESS, $1\frac{5}{16}$ IN. WORKING PRESSURE, 250 LB. PER SQ. IN.

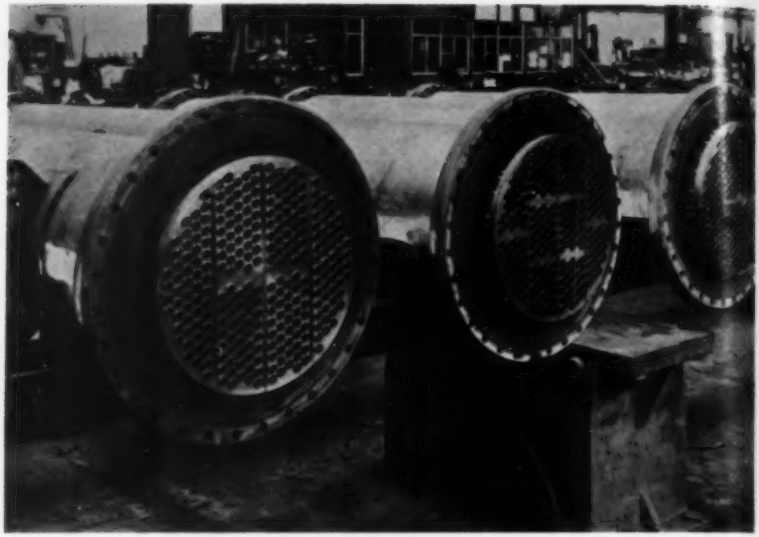


FIG. 18.

THREE OF A LARGE NUMBER OF HEAT EXCHANGERS MADE BY MESSRS. BABCOCK & WILCOX, LTD., FOR AN OIL REFINERY. THESE VESSELS HAVE WELDED SHELLS AND THE PHOTOGRAPH SHOWS THE TUBE BUNDLES PARTIALLY WITHDRAWN.

FIG. 19.

FUSION-WELDED REACTION CHAMBER MADE BY MESSRS. BABCOCK & WILCOX, LTD. DIAMETER, 2 FT.; LENGTH, 15 FT.; PLATE THICKNESS, $1\frac{3}{4}$ IN.

collapse at a temperature slightly above the upper critical. The question might well be asked as to the grounds on which this apprehension is based, as there is little published evidence of the actual distortion which has occurred in cylindrical vessels subjected to this treatment.

The author suggests that, in order to obtain the best condition of ductility in combination with toughness, the normalizing heat treatment should be followed by reheating to 600–650° C. and cooling in a still atmosphere or in the furnaces.

The usual practice in regard to the heat treatment of pressure vessels is to subject them to what is termed a "stress relieving" treatment. This involves heating the vessel in a furnace to a temperature of between 500° C. and 650° C., depending on the requirements of some particular specification, or, in many cases, on the usual practice of the firm concerned.

In the author's opinion this practice is quite satisfactory for welded pressure vessels made from low-carbon mild-steel boiler plate, and whilst it is difficult to assess the magnitude of residual stress and the degree of stress relief afforded, there is no question that satisfactory results are being obtained by stress relieving at 600–620° C.

The idea of relieving stress by mechanical straining is based on the theory that the plastic flow which takes place when steel is strained above the yield point will even out local stresses which may be locked up therein. The question is receiving attention by a number of research authorities, and at the moment it cannot be regarded as a desirable proposition for welded pressure vessels.

Testing and Inspection.

The author dealt fully with this subject in a paper given in Group 4 of the Welding Symposium published by the Iron and Steel Institute. It will be appreciated that this subject is too big to be dealt with adequately in a brief sub-section of the present paper. It is in the sphere of testing and inspection that the functions of Lloyd's Register are mainly concerned. Reference has already been made to the "Tentative Requirements for Fusion Welded Pressure Vessels intended for Land Purposes" published in July, 1934, and since that date a considerable number of vessels have been constructed under survey. As regards marine work, definite rules have not yet been laid down, the present rules have, however, been amended, so as to permit consideration being given to proposals involving the fitting of fusion-welded pressure vessels on board ships classed with the Society. Such cases are at present dealt with on their individual merits, but in general the terms of the above-mentioned "Tentative Requirements" are applied.

The first difficulty which arises in the adoption of a testing and inspection procedure is the grading of pressure vessels in the order of their importance and vulnerability, *e.g.* it would be quite unreasonable to apply the same tests to a low-pressure unfired water container as would be applied to a high-pressure boiler drum.

Lloyd's Register consider pressure vessels under two heads, namely:

Class I.—Fired pressure vessels and vessels subject to internal steam pressure above 50 lb. per sq. in.

Class II.—Pressure vessels not included in Class I.

A clause is included in the "Tentative Requirements" which permits of a certain elasticity in the application of the above definitions.

In view of the variety of pressure vessels now being welded, it appears necessary that a more precise classification should be made, and the test requirements graded accordingly; this, it may be stated, will shortly be done, when the rules are revised.

The welding of the highest class of pressure vessels—namely, high-pressure boiler drums, autoclaves, etc.—is a specialized branch of the welding industry. The work is of such importance that, so far as Lloyd's Register is concerned, Class I pressure vessels can be accepted only provided they are made by approved firms who have carried out a comprehensive series of special tests to demonstrate the consistency and quality of their welding work.

The routine testing of pressure vessels involves the welding up of sample test plates conjointly with the welding of the longitudinal and circumferential seams. For the former it is usual to attach the sample test plates at the ends of the seams, so that the sample joint forms a continuation and duplication of the seams. This arrangement has sometimes been criticized, and doubts have been expressed as to whether the test plates comprise a true sample and reproduction of the actual seam. The author recently had tests carried out on specimens cut from a sample test plate, and also on specimens cut from the actual welded longitudinal joints. It so happened that the tests on the sample had indicated certain inherent defects in the weld, and this was confirmed by the tests made on the actual joint. This example affords an assurance that sample test plates welded conjointly with the joints of pressure vessels may reasonably be regarded as representative.

It is, of course, important that the heat treatment given to the test plates should be the same as that given to the pressure vessel itself.

For the purpose of the routine assessment of the quality and strength of the welded joint, it has been found satisfactory to rely upon a series of simple and straightforward tests, namely :—

1. All weld tensile.
2. Transverse tensile, across joint.
3. Transverse bend, across joint.
4. Impact tests in weld and fusion zone.

For Class I pressure vessels, in addition to these tests it is necessary to carry out density tests and to take photomicro- and macro-graphs of a section of the weld. The microscopic examination must include the centre of the weld and the fusion zone. Further, the entire length of each of the welded seams must be subjected to X-ray examination, and finally, satisfactory results must be obtained from the application of the appropriate hydraulic and hammer tests to the finished vessel.

It is considered that with this testing procedure, combined with a very careful inspection at various stages in the construction of a pressure vessel, the production of a safe and reliable welded structure will be assured.

Conclusion.

The subject of the fusion-welding of pressure vessels involves the consideration of so many important details that in a brief paper such as this it is not possible to do justice to the subject as a whole. It is thought, however, that the foregoing notes will serve the purpose of bringing to the notice of the members of the Institution of Petroleum Technologists some of the facts concerning the application of fusion welding to pressure vessels and the present position regarding development.

THE USE OF WELDING IN TRANSPORTATION AND STORAGE OF OIL.*

By A. C. Hartley, A.C.G.I., M.Inst.C.E., M.I.Mech.E. (Member), and A. C. Vivian, B.Sc., A.C.G.I., A.M.Inst.C.E. (Associate Member).

Early Uses of Oxy-Acetylene Welding.

Welding was used in some few instances and to a very limited extent in connection with the transport of oil before 1926, but it was in that year that this method of making joints was first adopted in place of screwing joints in main trunk lines, and the oxy-acetylene process was used.

The first type of joint was made by forming a socket on one end of the pipe to receive the plain end of another pipe; a fillet weld was made between the end of the socket and the wall of the pipe.

This was not entirely satisfactory, and a rib was rolled on the plain end of the pipe to form with the end of the socket a groove in which to lay the weld metal. Many variations were made in the dimensions and clearances of the socket and rib in endeavours to improve the strength of the joint. There was, however, difficulty in getting sufficient penetration into the wall of the pipe with a fillet weld, and when any bending of the pipe-line occurred, the end of the pipe was liable to use the bottom of the socket as a fulcrum, and severe stresses were imposed on the fillet weld, frequently causing fracture of the joint. Nevertheless, even in these early days welded joints proved as satisfactory as screwed joints, and the use of welding grew apace.

The equipment required for oxy-acetylene welding, with its oxygen cylinders, acetylene generators, water requirements, etc., proved awkward and expensive to transport along the right-of-way in the difficult country through which many pipe-lines had to be built.

Electric Arc Welding.

Meanwhile, however, electric arc welding was being developed, and efforts were made to adapt its use to pipe-line conditions, particularly in view of the fact that gasoline engine-driven electric-generating sets only required gasoline, which had in any case to be provided for transport, apart from electrodes.

Bare-wire electrodes were first used, but the welds proved to be brittle, and also liable to excessive corrosion.

Steps were taken to improve the quality of the welds by using improved types of electrode, of the "slag"-protected type, and later of the gas-protected type, and a combination of both types.

Meanwhile, further designs of joints were experimented with for use with

* Paper presented for discussion at the One Hundred and Sixty-ninth Meeting of the Institution of Petroleum Technologists, February 11th, 1936.

both the oxy-acetylene and electric welding processes, and by 1931 the "double-bell" and inner "sleeve" or chill-ring type had become almost universal. This type was expensive, but enabled comparatively unskilled operators to produce a very reliable joint at an increased rate.

Fig. 1 shows a screwed joint and a double-bell welded joint placed alongside one another for comparison purposes.

Meanwhile, with the increasing use of electric welding, the oxy-acetylene progress had not stood still, and great improvements had been made by introducing the carburizing flame and the semi-automatic and automatic welding heads.

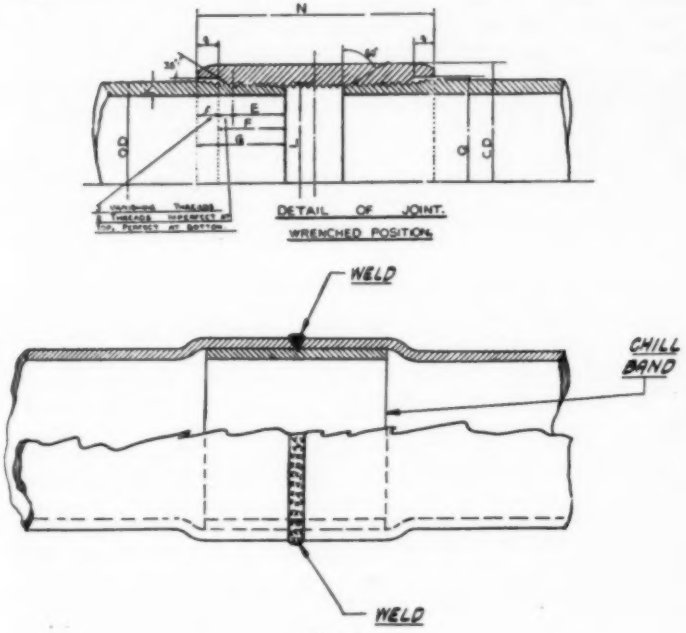


FIG. 1.

Both systems of welding have been developed to a high state of efficiency, and there is little to choose in the quality of the welds produced, although the convenience of the electric arc welding equipment referred to above has resulted in its adoption in the greater number of cases.

METHOD OF JOINTING.

The usual procedure in the field is to use as long lengths of pipe as possible, 40 ft. or even 45 ft., and place as many lengths on dollies (designed to permit of easy rotation of the pipe) as the right of way will permit in one straight line. It will be realized that joints can be more rapidly and more reliably made when the pipe can be rotated to allow the welder

to work downhand than when a joint has to be made to a pipe already fixed in position, and vertical and overhead welding is necessary. Efforts are therefore made to have as many " roll " welds and as few " tie-in " or " bell-hole " welds as possible.

The welder first tack welds the joints of the pipes on the dollies by welds about 1 inch long at four places on the circumference. He then welds half the joint with the stringer head or first run of smaller size electrode, while the helpers rotate the pipe. He moves along doing half of each joint in turn until he reaches the last joint, and then returns along the line doing the remaining half of each joint. Meanwhile the helpers follow, and carefully remove the slag in preparation for the next run.

The welder then completely finishes each joint with the finish head or second run of larger size electrode. By doing the first run in two halves and the last in one, he is able to start at the beginning of each length and finish at the far end in position to start on the next length without waste of distance and time in unnecessary movement of equipment.

After completion of the roll welds, the whole length of pipe is dragged, usually by tractor cranes, on to supports over the trench, and the tie-in or bell-hole weld is made. Smaller-diameter electrodes and three or more runs are used to facilitate vertical and overhead welding.

Repair Work.

The electric arc had become established by 1929 as a convenient means for repair work, and corrosion pits were regularly filled up with welding metal while the oil was flowing in the line. The electric arc was also extensively used for the repair of leaking collars by welding round their edges.

Various types of split sleeve made from larger sizes of pipe were also devised for entirely enclosing leaky screwed joints or weak sections of the pipe.

Fig. 2 shows such a sleeve used for repair of leaky screwed joints. The upper photograph shows the partial assembly, and the lower the completely welded-up repair.

At about this time experience showed it to be better, where pipes were badly corroded, to cut out entire lengths, bevel the ends and re-joint by plain butt welds. This method was found to be satisfactory when the correct angle of bevel and amount of " flat " to be left had been established.

Plain Butt Welds.

In the case of 8-inch pipe, 0·277 inch thick, the best results were obtained with a bevel forming an included angle of 80°, and with a $\frac{1}{32}$-inch " flat " on the end of each pipe. The pipes were lined up with their ends $\frac{1}{8}$ inch apart in suitable line-up clamps and were tack-welded at four points. The first bead was applied with $\frac{1}{4}$-inch electrodes, using 300 amperes current, followed by two more beads with $\frac{5}{16}$-inch electrodes, using 400 amperes in the case of the " rolled " welds. Three beads with $\frac{3}{16}$-inch electrodes were used for the " bell-hole " welds.

Three beads have been used in such circumstances, chiefly to enable the

weld metal to be built up above the surface of the pipe, and so compensate for any possible lack of penetration at the bottom of the bead which might arise from the desire to avoid any possibility of icicles inside the pipe.

Welding had produced very great economies in pipe-line construction, and during the days of the depression, when it was necessary to save all possible cost, efforts were made to get down to the simplest form of joint. The plain-butt type developed in repair work was adopted for new construction, and the expense of belling and of providing inner sleeves was thus avoided. The simplest and cheapest possible form of joint has thus become established.

Reduced Thickness of Pipe.

It was soon realized that thinner pipe could be used when welded joints were adopted, as it was unnecessary to make any allowance for the metal cut from the walls of the pipe in forming the screwed thread. As an example, it may be stated that in one main pipe-line, 12-inch-diam. system the pipe was of 0·375 inch thickness when supplied with screwed joints, but further lines in this system are now being laid with welded joints, and pipe of 0·330 inch thick has been used, the cost of pipe f.o.b. being reduced by 20 per cent.

In the case of this 12-inch pipe it was originally planned to supply pipe ends bevelled to form a 60° included angle, with $\frac{1}{16}$-inch flat, and to weld up the pipe with about $\frac{1}{8}$ inch between the ends. As a result of further experience, the pipe was supplied with the ends bevelled for an included angle of 90° and with $\frac{1}{16}$-inch flat as before, but the pipe ends were butted tight before welding. The greater included angle compensated for the elimination of a space between pipe ends and facilitated adequate penetration, while the tight butting prevented the possibility of "icicles" being formed inside the pipe during welding.

The cumulative effect of these developments has been so to reduce the cost of the larger sizes of welded lines that it has now proved economic, and it is the regular practice to replace old 6-inch, 8-inch and 10-inch screwed lines by a single welded line of equivalent capacity. The recovered pipe, after reconditioning the bevelling for welding, is used for gathering systems and in refineries.

Reliability with Speed.

Welded lines have proved entirely reliable, and have enabled higher pumping pressures, with consequent considerable economies, to be safely adopted. As an instance it may be stated that in a recent trans-desert line upwards of 180,000 welds were made in record time, and only two or three slight "weeps" have been disclosed during test and subsequent operation. One of the chief items of cost in the building of most trunk lines is the maintenance in the field of the elaborate organization of welding crews, labour, equipment, workshops, commissariat, transport, etc., and every day saved by increasing speed of operation is of the highest importance.

In order to achieve this high speed of operation, larger sizes of electrodes with higher welding currents have been progressively used, and electrodes

of $\frac{5}{32}$-inch diameter with welding currents as high as 400 amperes are now regularly used.

The procedure of welding pipe-lines previously referred to is illustrated in Figs. 3, 4, 5, 6 and 7. The usual length of pipe as delivered from the manufacturers is 40 ft., and as many lengths as practicable are lined up on "dollies," and tack welded at four points around the circumference. The pipe is then rotated by means of a chain clamp, as shown in Fig. 3. Fig. 4 shows a close-up of a welder at work on a rolled joint, and Fig. 8 shows, by way of contrast, a pipe-screwing gang at work making a screwed joint. Fig. 5 shows a "bell-hole" weld being made with the pipe supported above the trench. In some cases the pipe may be welded in the trench, in which case it is necessary to excavate around the position of the joint to enable the welder to work. Fig. 7 shows a dolly, designed to enable the pipe to be rotated without difficulty during the making of rolled joints.

Fig. 6 shows the type of clamp used for lining up pipe to hold the pipe ends in their correct position for tack welding. This clamp is required where plain-ended pipes are welded together, and whereas it is obvious that some additional labour and time are involved in using the clamp as an alternative to the double-belled end and sleeve joint, which aligns itself, it has been found to be cheaper on account of the reduced f.o.b. cost of the pipe.

A further advantage of eliminating the "belled-end" type of joint and replacing it by the plain butt weld is that the wrapping of the pipe is greatly facilitated. Fig. 9 shows a pipe-wrapping machine at work.

At one time reinforcing straps were used across butt joints, but their use was found to be unnecessary and, if anything, a disadvantage. The metal in the weld with the latest type of electrode has proved to be at least as immune from corrosion and as good in tensile strength and ductility as the pipe itself.

It should be mentioned that butt-welded joints are "reinforced," *i.e.* weld metal is built up to a slightly greater diameter than the outside diameter of the pipe, in order to compensate for any lack of penetration which may occur by reason of the care taken to prevent icicles forming inside the pipe. The reinforcement makes the strength of the joint greater than the strength of the pipe itself.

It is very necessary to ensure that welders are competent in the first place, and to prove that they retain their efficiency by regular tests.

Testing of Personnel.

In order to test the work of the welders it is common practice for inspectors to have coupons or longitudinal specimens cut from the pipe joint with the butt weld at the centre. These are then tested in a portable tensile testing machine. For routine tests of welding a good test is to take two pieces of pipe, tack weld them in line in a horizontal position to the bench, and then to weld the joint between the two pieces of pipes, this welding constituting in effect a "bell-hole" joint. Four equally spaced coupons are cut from the pipe diametrically opposite, and a bend test and tensile test made. A visual examination of the joint is also made by saw cutting through part of the weld in each of two of the coupons and hammering off.

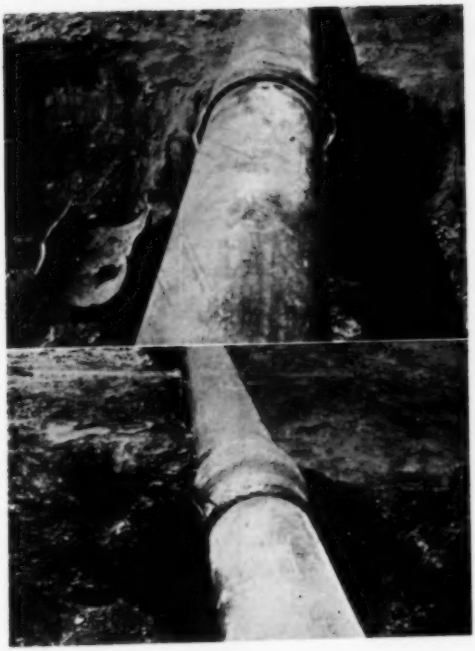
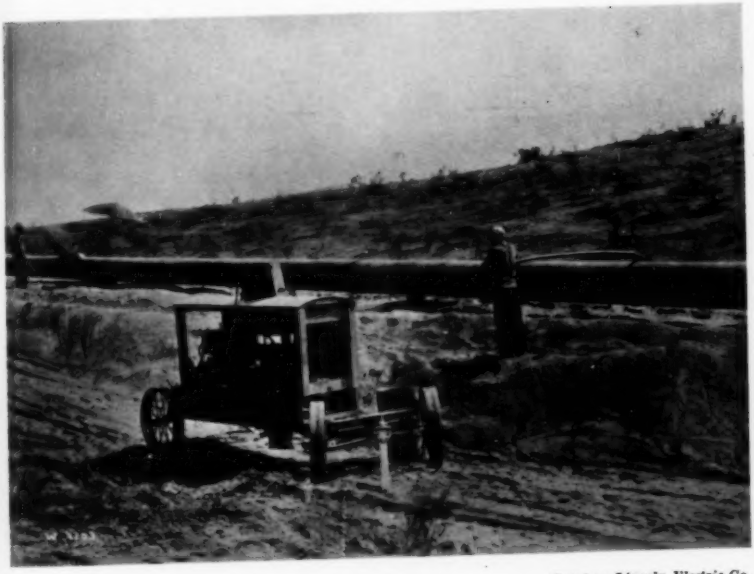


FIG. 2.



Courtesy Lincoln Electric Co.

FIG. 3.

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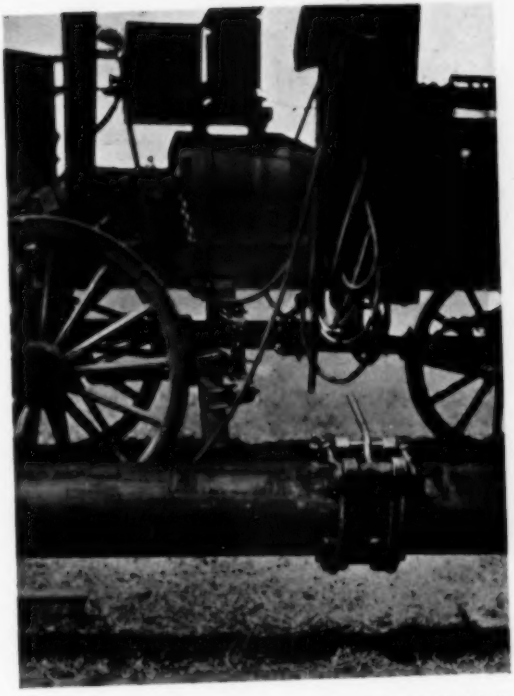
Courtesy Lincoln Electric Co.

FIG. 4.

Courtesy Lincoln Electric Co.

FIG. 5.



Courtesy Lincoln Electric Co.

FIG. 6.

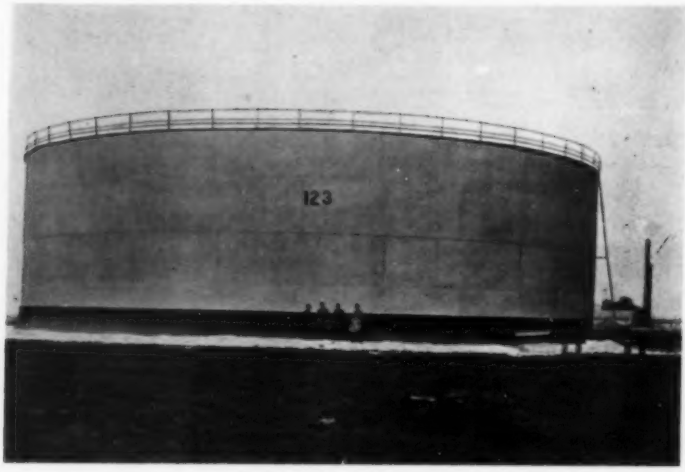
Courtesy Lincoln Electric Co.

FIG. 7.

FIG. 8.

FIG. 9.

FIG. 10.



Courtesy Quasi Arc Co.

FIG. 11.

Lay-out of Welded Lines.

The reliability of welded joints has enabled isolating valves previously used every few miles along a pipe-line to be eliminated, and another source of weakness has been thereby removed. These isolating valves are essential in the case of screwed lines to localize the effects of a failure and to facilitate repairs without shutting down the whole system. In some cases valves have been designed for welding directly to the line. Their use has further reduced the number of flanged and screwed joints to a minimum, thus making pipe-lines almost a continuous steel pipe with joints equal in strength to the pipe itself. It has, in fact, been found that failures occur more often in the pipe than in the welded joints. Expansion joints are not necessary in 12-inch and smaller pipe, but the procedure commonly adopted is to crowd pipe into the trench by removing intermediate supports at the coldest part of the day. The parts in the trench are buried and the intermediate parts forced in by tractors or other means after removal of the remaining supports. If sufficient pipe is crowded in to provide the length required under the coldest condition, no fear need be entertained of pull outs, and on expansion the pipe will " snake " across the trench. Where pipes are not buried, it has been found good practice to " stagger " them. Fig. 10 shows a picture of a staggered line. Considerable movement takes place, due to the difference between day and night temperatures, but flexibility of the pipe is sufficient to prevent any failure at the joints, particularly when welded.

It will be noted that sharp bends or kinks are made at equal intervals of about 200 ft. This method has proved effective in making each section of pipe take care of its own expansion and contraction, and preventing movements being communicated from section to section, as happens when gentle bends are used. These movements are usually in the same direction, and when permitted accumulate over long lengths, with the inevitable result of a pull out.

Pipe Manufacture.

No mention has yet been made of the equally important advantage to the industry of the adoption of welding methods in the manufacture of pipe. Manufacture of the old lap welded pipe was replaced by the introduction of automatic means for electrically welding the longitudinal joints of pipe. Large quantities of fusion welded pipe have also been made.

It is true that seamless pipe has now replaced electric welded pipe in the sizes used for oil, but the larger diameters used for gas are generally electric arc welded.

Grade of Steel.

The A.P.I. Grade " B " of steel is largely used for pipe for welding with a 0·3 carbon content. It has been found to be desirable to keep to this limit of carbon to ensure ease of welding in the field.

Storage Tanks.

While pipe-lines provide the most striking examples of the usefulness of welding in transportation of oil, welding has also been put to considerable

advantage in the construction of storage tanks. Fig. 11 shows a tank built by the Medway Oil and Storage Company, Ltd., Isle of Grain, Kent, who have built fifteen tanks varying in size from 75,000 galls. to 3,000,000 galls. capacity.

In some cases riveting has been adopted for side plates, welding being confined to the bottoms and roofs. In particular, welding has proved a great advantage in the repair of existing tankage. Corroded bottoms of tanks are nowadays repaired by laying a new tank bottom on a layer of inert material and lap welding the plates, and connecting to the tank side. In the case of tanks for the storage of light spirit, the floating roof has enjoyed great vogue on account of its practical elimination of losses from vaporization, and welding has considerably simplified the construction of these roofs.

In the case of tanks for storing light spirit under pressure, welding has replaced riveting to a considerable extent—for example, a number of Hortonspheroids of $2\frac{3}{4}$ million gallon capacity have been built throughout by the electric arc process.

Welding is now also very extensively used for manifolds, service piping around pumping stations, and, in the latest practice, steel valves have been designed and bevelled for welding direct into the pipe-line, thus eliminating screwed and flanged joints to a large extent around pumping stations.

Electric Welding Equipment.

In the past there has been divergence of opinion as to the relative merits of alternating current and direct current for welding purposes, but there is no doubt that future experience will show that for many of the applications alternating-current welding can be just as satisfactory as direct-current welding.

In general, the following is a brief list of electric welding equipments :—

(1) Petrol engine driven D.C. generators.

(2) Diesel engine driven D.C. generators.

(3) Motor generator sets having A.C. motor driven from the mains and D.C. generator providing the required welding current.

(4) Transformer welding sets which are connected to power mains and give the necessary supply for A.C. welding.

Again, a great deal of discussion has taken place as regards the merits of single-point welding as against multiple-point welding. In this connection it may be stated that whereas in special cases it may be essential to have single-point welding, there is no doubt that multiple-point welding, both D.C. and A.C., will continue to be used to a great extent. It is possible that in the past one has been inclined to attach too much importance to the special nature of the current required, whereas future experience may determine that, given the proper melting arrangements, *i.e.* using either A.C. or D.C., satisfactory work can be carried out.

In the case of gasoline sets, generators having an output of 300 amps. or 400 amps. are usually employed for pipe-line work. In the case of large pipe-lines the 400-amp. sets are used for rolling joints and the 300-amp. sets for bell-hole joints. With such equipment it is of great importance

that the engine is given a much higher horse-power rating than the generator, as experience has shown that with most welding sets manufactured in this country, the gasoline engine has been considerably under-rated, and may collapse after a short period when engaged on actual welding work.

Furthermore, it is found that these equipments, when being transported from place to place, are liable to considerable damage from loose connections in the generators, switchboards, etc., and it is now standard practice to fit the equipments on a sprung carriage with pneumatic tyres and provide same with a canopy.

The following table gives particulars of the rods dealt with by 300- and 400-amp. machines :—

$\frac{1}{8}$	inch dia. rods requiring	110	amps.
$\frac{5}{32}$	,, ,,	130	,,
$\frac{3}{16}$	,, ,,	200	,,
$\frac{1}{4}$	,, ,,	275	,,
$\frac{5}{16}$	,, ,,	375	,,

The 400-amp. machines will deal with $\frac{5}{16}$-inch and $\frac{3}{8}$-inch rods and provide ample capacity for jobs where a long cable from welding set to work is required. Gasoline sets, especially for pipe-line work, should be mostly in the 400-amp. range.

With reference to the diesel-driven generators, no great experience is yet available as regards the operation of the diesel engine and the welding conditions.

Motor generator sets for general tank and pipe work should again be of the 300 or 400 amp. size. These should also be fitted on a sprung chassis with pneumatic tyres, and when used in the open provided with a canopy.

As regards transformer sets, their operation is entirely static, and they can be obtained in the various sizes suitable for general construction and repair work.

Considerable improvement in the design and portability of this class of welder has taken place over the last few years, and it is possible that A.C. welders will in future be used to a much greater extent than in the past.

The various auxiliaries for use in connection with welding require careful consideration, and special attention should be given to the electrode cable. This cable should be of such design and construction as will permit of the proper and easiest possible manipulation of the electrode holder during the welding process. The greater the flexibility the less fatigue will be experienced by the operator from the handling of the arc. In general, about 30 feet of electrode cable should be allowed per electrode holder, and as an example as regards flexibility, it is mentioned that for 400 amps. the flexible cab-tyre cable should have approximately 3250 strands. This ensures the extra flexibility required.

As regards electrode holders for pipe-line and such work, it is usual to standardize on one holder which is suitable for currents up to 300 amperes, and on another size of holder suitable for currents above 300 amperes. It is important to keep in mind, with reference to the design of the holders, that there may be times when these must be manipulated in very confined spaces. In general, it has been found that a proper designed electrode holder can save much of the operator's time.

Another important item is head-shields. These should be light and well ventilated, and comfortable. The shields should be well back and close to the head, preventing flashes from other operators. The design should be such that it can be easily thrown back off the head to allow of inspection of the work.

Experience has shown that only lens of the highest quality should be used in welding. It will be appreciated that the energy given out by a high-intensity arc embraces all types of radiation, including infra-red rays, visible rays and ultra-violet rays, and consequently only glasses should be used the ray absorption of which is very carefully worked out.

It is important in the case of welders' gloves that only mittens with seams specially stitched to stand hot metal spatter should be used.

Various methods have been tried out for the purpose of testing welds to ensure that these are entirely satisfactory and will meet all requirements. In this connection considerable use is now being made of X-ray equipment for the purposes of examining the welds. Such equipment has many advantages, as, apart from indicating clearly any faulty welds, this information is obtained without the necessity of having to damage or break up any of the work.

It will be seen that those responsible for the transportation and storage of oil have not been slow to adopt each improvement in welding method as it has been produced, with consequent great advantage to their enterprises from the point of view of reduced first costs, greater reliability, and an enormous reduction in maintenance costs.

THE TRAINING OF ELECTRIC WELDERS.*

By W. G. Poole and R. T. Rolfe.†

The art of electric welding, although regarded by many as of comparatively recent growth, goes back as far as the year 1885, when the first patents were taken out in England, the specifications covering the welding, cutting and perforation of metals. From that time onwards, various improvements were made in electrodes, apparatus, etc., but for a long period few serious investigations were made into the uses and applications of welding, which was usually regarded, indeed, only as a last means of repair of machine parts which would otherwise be scrapped. It was really not until the War that its use became extended, and then the urgency of repairs made its employment often artificial and uncommercial. It did, however, demonstrate the value of the process under such conditions, and, after the conclusion of hostilities, it was interesting to speculate as to its development and use in purely industrial directions. If, as an obvious field for the newer process, welding was to replace riveting, then welding must be as certain as riveting in the strength obtainable from joints thus made. It would be quite useless to claim for welding a pre-eminent position, simply because it *could* give results superior to riveting, if on occasion it was inferior. The actual progress made and the technical efficiency achieved have resulted, however, in the complete justification of the process, and the confidence now placed in it has caused the wide replacement of riveting by welding in steel structural work of all kinds. The astounding development of the craft was reflected in the Symposium on the Welding of Iron and Steel recently arranged by the Iron and Steel Institute and some eleven other technical societies, when some one hundred and fifty papers were received, covering many different aspects of the matter.

The fact that the application of welding is now so wide, of necessity brings to the fore the workman responsible for the making of welds, and it is scarcely necessary to say that the success of any industry depends to a very considerable degree on a constant supply of trained operators. Particularly is this necessary in welding, not only because it is an industry which has only comparatively recently been developed, but also because it presents peculiar difficulties. These difficulties are not only those involved in training, but attend every phase of the industry, and they are due chiefly to the fact that the assessment of quality in welding is a somewhat difficult matter. Thus, while the quality of many operations is obvious on inspection, that of a weld cannot be so appraised. It is, of course, easy to judge, from the smoothness and evenness with which the metal has been deposited, that the operator in question has done a good deal of welding; and surface finish is naturally important as a selling point.

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* Paper presented for discussion at the One Hundred and Sixty-ninth Meeting of the Institution of Petroleum Technologists, February 11th, 1936.

† W. H. Allen, Sons & Co., Ltd., Bedford.

It is possible, however, although perhaps less likely, to have a weld which outwardly appears excellent, but which is nevertheless a poor one, because of a concealed defect in the actual joint. This, of course, is often due to lack of penetration, which is due in turn to lack of experience on the part of the operator.

Requirements for Good Practice.

There are various fundamental requirements of good welding practice, some of which are matters of simple common sense. For example, in the fabrication of a large engine frame, as in the case of the large Combination Bedplate for a Diesel Engine and Dynamo, shown in Fig. 1, or other

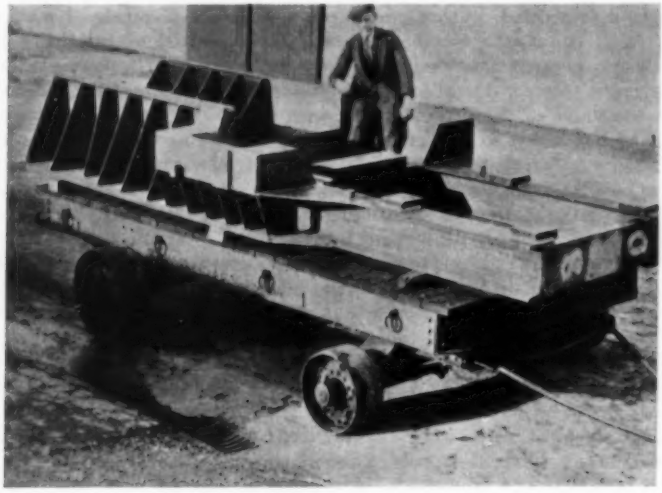

Fig. 1.

COMBINATION BASE-PLATE FOR DIESEL ENGINE AND DYNAMO.

intricate piece of welded machinery, it is necessary to make the joints in a definite order, or severe distortion will be caused by the stresses set up during heating and cooling. This distortion will be found after the welding has been completed, but will often be intensified after machining, when the removal of some of the material permits the latent stresses set up in welding to produce further distortion. This can, of course, be corrected by heat-treatment after welding and before machining, a method often employed, but this does not relieve the welder of the necessity of making a fabric which is as correct as possible to the desired dimensions. Fig. 2 is a diagrammatical representation of the distortion in the fabricated frame of an 8-cylinder diesel engine, both after fabrication and after further heat-treatment, this being effected by slowly raising to 600° C. in 4 hours, allowing to remain at this temperature for 1 hour, and then cooling slowly.

The dimensions after this treatment are shown in all cases under those of the bedplate as fabricated, and in thinner type. It may be said that a further similar treatment, but at 850° C., produced no further change in dimensions, showing that complete stress release had been effected at the lower temperature. Success in fabrication involves a precise knowledge of the way in which the fabric is likely to be stressed during the welding, and demands considerable experience in the construction of similar work, for it cannot be obtained from text-books. A further important point is involved in the making of the actual joint, where success cannot be obtained by merely filling up the gap with weld metal. It is necessary, in addition, to melt some of the parent metal, thus avoiding what is known

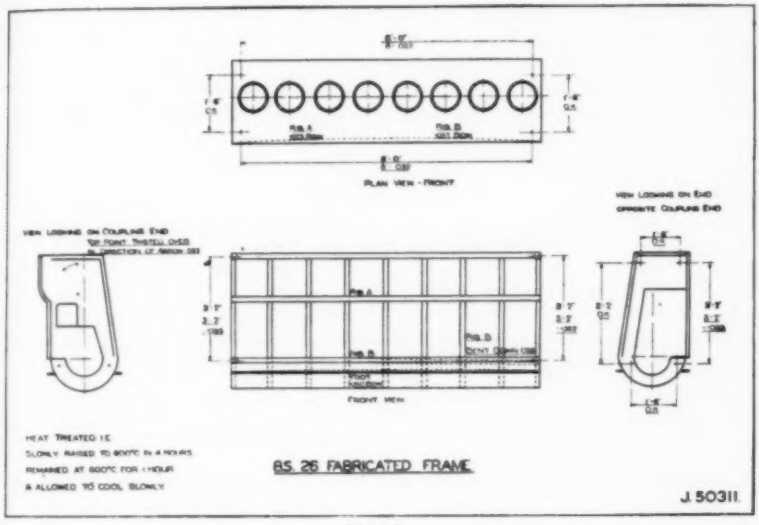
PLAN VIEW - FRONT
FRONT VIEW
HEAT TREATED IE
SLOWLY RAISED TO 600°C IN 4 HOURS
REMAINED AT 600°C FOR 1 HOUR
& ALLOWED TO COOL SLOWLY
BS. 26 FABRICATED FRAME
J.50311

FIG. 2.

DIMENSIONS OF LARGE FABRICATED FRAME BEFORE AND AFTER HEAT-TREATMENT.

in foundry practice as a "cold shut," and ensuring at the same time that the transition between parent metal and weld metal shall be as gradual as possible. Here various matters are involved, such as the composition of the electrode in relation to that of the job, the current strength, and, particularly, the technique of the operator. Where, as usual, a number of runs are necessary to complete the joint, the slag found on the surface of each run must be effectually removed before the next run is made, a matter where experience and care on the part of the operator are essential. It cannot be too strongly emphasized that these defects are largely hidden, and even if one has ensured that all welders have received adequate instruction, and also makes at intervals such tests as will verify the general quality of the work of each operator, there is always the danger of an occasional bad weld being made. In most cases, it is only possible to determine that a weld is inferior by X-ray examination, sometimes by a

magnetic test, methods which, although applicable in some special cases, cannot generally be employed for routine work. Thus, one has always to rely to a considerable extent on the workmanship of the welder, and no pains should be spared to ensure adequate training, combined with such periodical testing as will guarantee the maintenance of quality. It is, of course, always assumed that one is using electrodes and plant of reputable quality. Even a good welder cannot be expected to make first-class welds with second-rate materials.

The Training of Welders.

Much of the knowledge and skill required in a welder would appear to be suitable for instruction in a technical school, and there are a number of firms which have their own schools for this purpose. This brings up the question of suitability and adaptability for the job. One finds, for example, that one boy will learn at least twice as quickly as another, and will turn out to be a much better welder in the long run. While the authors have

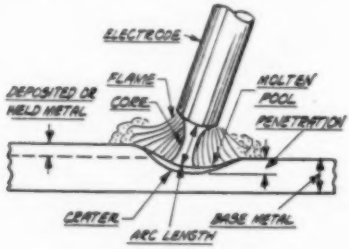

Fig. 3.

DIAGRAMMATIC SKETCH OF AN ORDINARY ARC IN PROCESS OF WELDING.

no special knowledge of vocational tests, it would appear that welding is an operation to which such methods might be applied with advantage. When selecting boys for training as welders, it must be appreciated how vastly welding differs from many other crafts—for example, moulding. The moulder has a multitude of operations to learn and perform, from the preparation of a simple cylindrical core to the complete moulding of a complicated pump. The welder, however, on the other hand, from the simple joining of two flat plates to the fabrication of an intricate frame, has always only one operation to perform, which he is for ever repeating. The lack of variety, therefore, and the consequent danger of monotony and staleness, must be strongly emphasized, because of their bearing on the selection of boys for training.

In the school, the raw youth is taught the fundamentals of his trade. It is impressed with the utmost force upon him from the outset that the human element plays a very great part in welding processes, and that to become a trusted and reliable welder he must cultivate an extreme conscientiousness in all he does. He must then learn the use of the equipment with which he will be provided and the means of protecting himself. Having thus far grasped what will be required of him, the embryo welder

can be introduced to such further matters as the differences between bare wire and covered electrodes, the use of the covering, the virtues of the shielded-arc electrode, the respective characteristics of A.C. and D.C., and the current required for different sizes of electrodes, etc. Here considerable use can be made of diagrams, as those shown in Figs. 3 and 4, which have been reproduced, with acknowledgment, from the *Procedure Handbook of*

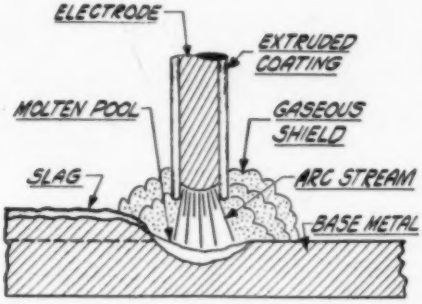

FIG. 4.

DIAGRAMMATIC SKETCH SHOWING SHIELDING OF ARC AND SLAG PROTECTION OF WELD METAL WHILE COOLING.

Arc Welding Design and Practice, published by the Lincoln Electric Co. Fig. 3 shows the mechanism of welding with a bare wire electrode. The base metal in the path of the arc stream is melted to form a pool of molten metal, which is forced out of the pool by the blast from the arc, so as to

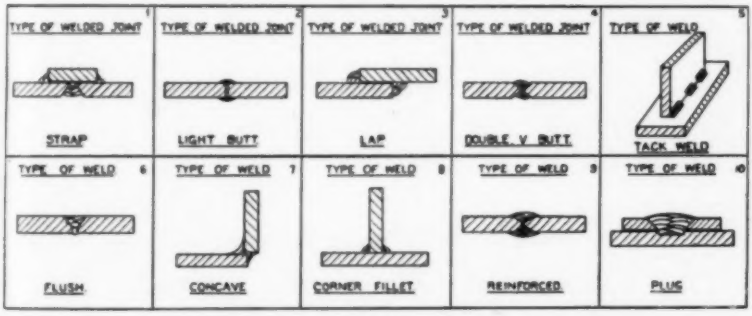

FIG. 5.

VARIOUS TYPES OF WELD.

form a small depression; while molten metal is piled up round the edges of the depression, which is known as the arc crater. The depth of this crater gives the penetration obtained in the welding, also showing to some extent the soundness of the weld. This depth, which depends to a considerable extent on the arc current and voltage, should be generally not less than $\frac{1}{16}$ in. Fig. 4 shows the mechanism of welding with a cellulose-

covered electrode, illustrating the slag covering, and the gas shield which envelopes the weld, and prevents contact of the atmospheric oxygen and nitrogen, thus resulting in the production of a weld of superior quality to that deposited by an ordinary arc. The apprentice welder must spend some time on theoretical work before he can be allowed to lay his first run, for he must appreciate the various kinds of welds and types of joints, as well as the methods of laying welds for given purposes, *e.g.* a strength weld

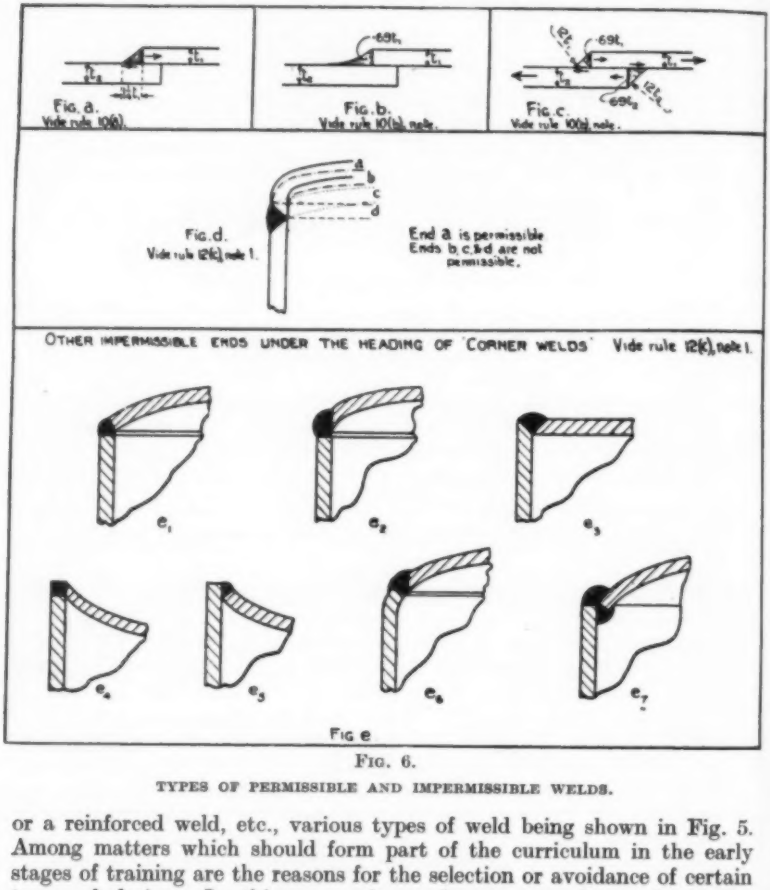
Fig. a.
Vide rule 10(a).
Fig. b.
Vide rule 10(b), note.
Fig. c.
Vide rule 10(c), note.
Fig. d.
Vide rule 12(k), note 1.
End a is permissible
Ends b, c, & d are not permissible.
OTHER IMPERMISSIBLE ENDS UNDER THE HEADING OF 'CORNER WELDS' Vide rule 12(k), note 1.
Fig e

FIG. 6.

TYPES OF PERMISSIBLE AND IMPERMISSIBLE WELDS.

or a reinforced weld, etc., various types of weld being shown in Fig. 5. Among matters which should form part of the curriculum in the early stages of training are the reasons for the selection or avoidance of certain types of design. In this connection, reference may be made to the Technical Report for the year 1928 of the British Engine, Boiler and Electrical Insurance Co., where a number of permissible and non-permissible welds are figured.

Some of these are shown in Figs. 6 and 7, the following notes referring to them having also been extracted :—

(*a*) With the fillet of a lap-welded joint, the surface of contact in tension shall extend over the full thickness (t_1) of the plate. The surface of contact in shear shall have a width of not less than t_1, and preferably not less than $1\frac{1}{4}\ t_1$.

(*b*) A fillet of a lap-welded joint shall by preference have a convex profile. At no time shall the thickness at the throat be less than 0·69 time the plate thickness (t_1).

(*c*) The throat thickness is defined as the minimum depth of the weld. (See Fig. *b*.) A minimum throat thickness of 0·69 t is equivalent to the radius of the fillet being not less than 12 t, which gives an approximately straight contour, the deviation from a straight line being only 0·02 t. (See Fig. *c*.)

(*d*) Relating to the attachment of dished ends, which are not allowed to be fixed by means of a corner weld, and, where a flanged end-plate is fixed

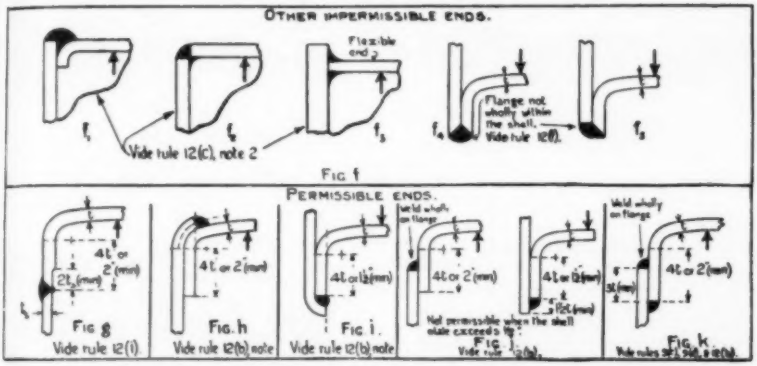

FIG. 7.

FURTHER TYPES OF PERMISSIBLE AND IMPERMISSIBLE WELDS.

by a butt joint, the flange shall form a continuous line with the shell plate. The term "corner weld" refers to any form of weld where the flange forms an angle with the shell plate, as illustrated in Fig. *d*.

(e_1–e_7) Any similar constructions without flanges, such as those shown in e_1–e_7, are also prohibited.

(*f*) Several other undesirable forms of end are constructed, *e.g.* those shown by Fig. 7, f_1 to f_5. These are not permissble, nor is any form of flexible end, the breathing of which imposes a direct bending stress on the weld.

(*g*–*k*) in Fig. 7 show various permissible welds.

(*g*) When a dished end of a thickness greater than that of the shell is affixed by a butt joint, the end of the flange shall be reduced to the thickness of the shell for a length not less than twice its thickness.

(*h* and *i*) With a dished end affixed by a lap joint, it is recommended that the end of the shell be constricted, and that the degree of constriction be not less than that shown by Figs. *h* and *i*.

(*j* and *k*) When a dished end is flanged, the length of the flange shall be

not less than 1½ in. for an end convex to the pressure, nor less than 2 in. with the end concave. The minimum length of the flange shall be at least four times the thickness of the plate.

Having so far progressed that his theoretical knowledge should now enable him to make his first practical acquaintance with a weld, the application of an oral test is advisable, to ensure that the boy has completely grasped the fundamentals underlying the art of welding. At last he may be permitted to make an actual weld, or rather he must first make several parallel runs on a flat plate, being instructed during the process on the length of arc to be maintained. Again, he must be taught to avoid over-current with its attendant under-cutting, or under-current with its tendency to lack of penetration, the weld being broken to show the operator faults which he must take steps to remedy. Where the necessary equipment is available, the taking of an X-ray photograph of the practice-weld will be of great assistance in enabling him to eliminate

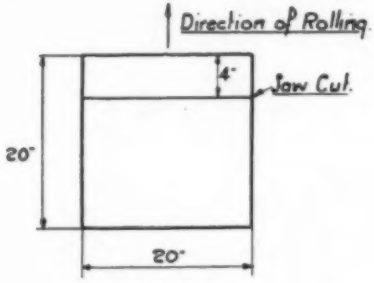

FIG. 9.

METHOD OF JOINTING PLATE USED IN PREVIOUS TESTS BY AUTHORS.

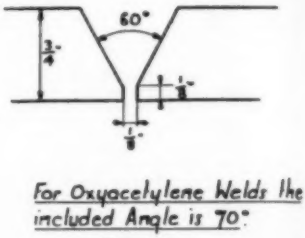

FIG. 10.

STANDARD V-JOINT WITH FLATS, USED IN PREVIOUS TESTS BY AUTHORS.

faults which would otherwise be perpetuated. Fig. 8 shows an X-ray photograph, made by Messrs. Philips Industrial X-Ray Service, of two each of welds made by four different welders, all these being reported by them to be of good quality. At the same stage he should also be introduced to the microscope, and should appreciate what it can reveal. Figs. 11–18 are of typical welds of the plate shown in Fig. 9, made by the use of different electrodes. This plate was ¾ in. thick and 20 in. long, and was sawn across transversely to the direction of rolling, at a distance of 4 in. from one end, as shown in Fig. 9, the sawn edges being bevelled and welded as in Fig. 10, using a single-V, of 60° included angle and with a ⅛-in. flat at the bottom. For the oxy-acetylene weld only, an included angle of 70° was used. Three runs were made, of electrodes nos. 10, 8 and 6, respectively, the weld being finished off, as usual, on the reverse side. The two pieces of plate were not held in any way during welding. The micrographs in Figs. 11–18 show four welds, at 20 and 100 diameters magnification, respectively, of the following :—

Figs. 11 and 12 : Fusion-Arc Weld made with slag-coated electrode.
Figs. 13 and 14 : Oxy-Acetylene Weld.

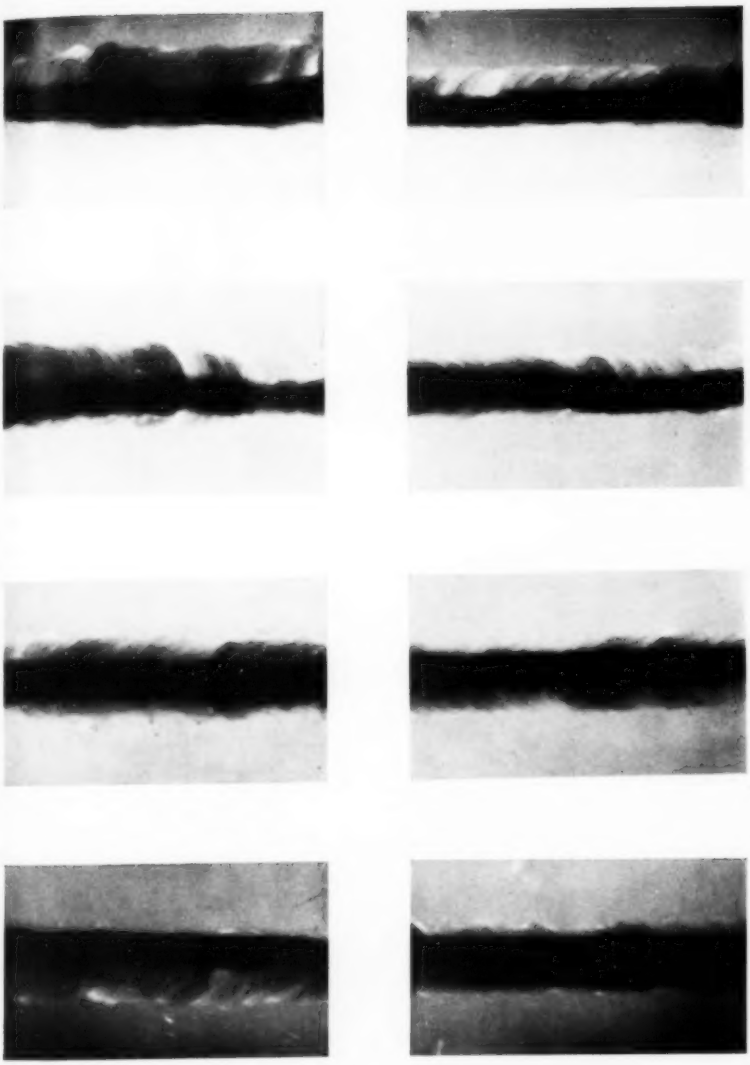

FIG. 8.

TYPICAL X-RAY PHOTOGRAPHS OF PLATE WELDS.

(*To face p.* 240.

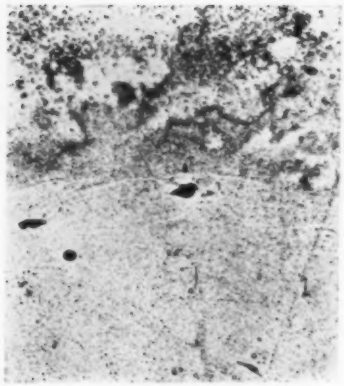

FIG. 11.
WELD MADE WITH SLAG-COATED ELECTRODE. × 20 diam.

FIG. 12.
WELD MADE WITH SLAG-COATED ELECTRODE. × 100 diam.

FIG. 13.
OXY-ACETYLENE WELD. × 20 diam.

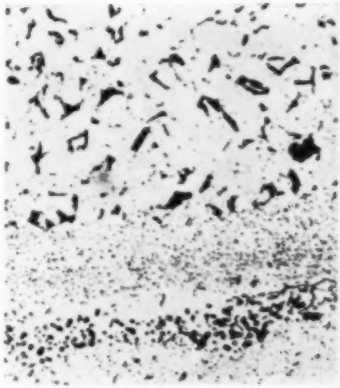

FIG. 14.
OXY-ACETYLENE WELD. × 100 diam.

(Microphotographs reduced to four-fifths linear in reproduction.)

FIG. 15.

WELD MADE WITH BARE-WIRE ELECTRODE.
× 20 diam.

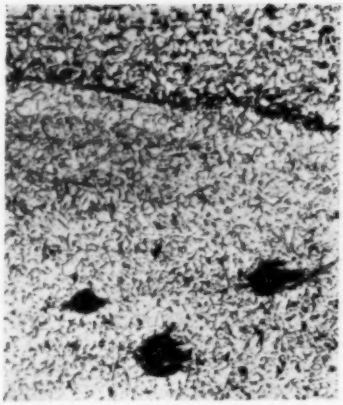

FIG. 16.

WELD MADE WITH BARE-WIRE ELECTRODE.
× 100 diam.

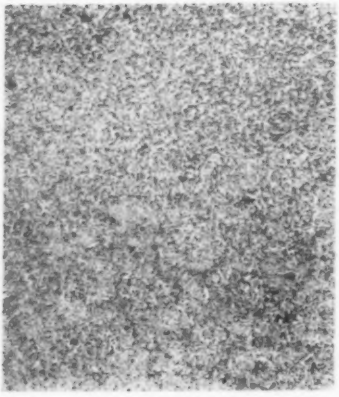

FIG. 17.

WELD MADE WITH CELLULOSE-COVERED ELECTRODE (SHIELDED-ARC TYPE).
× 20 diam.

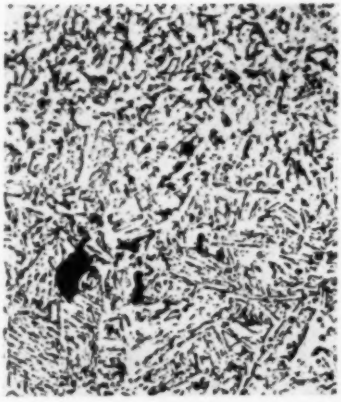

FIG. 18.

WELD MADE WITH CELLULOSE-COVERED ELECTRODE (SHIELDED-ARC TYPE).
× 100 diam.

(Microphotographs reduced to four-fifths linear in reproduction.)

6"
6"

Figs. 15 and 16: Fusion-Arc Weld made with bare wire electrode.
Figs. 17 and 18: Fusion-Arc Weld made with cellulose-covered electrode.

The top portion of each micrograph shows the parent metal, and the bottom that of the deposited metal. The large inclusions in the bare wire welds (Figs. 15 and 16) should be noted; and also the excellent quality of the welds made with gas-shield electrodes (Figs. 17 and 18). In the last case, the line of demarcation between parent metal and weld metal is almost indistinguishable, such an effect being always indicative of good mechanical quality.

Having mastered the art of obtaining and maintaining an arc of correct length, the apprentice welder may proceed to the different positions of

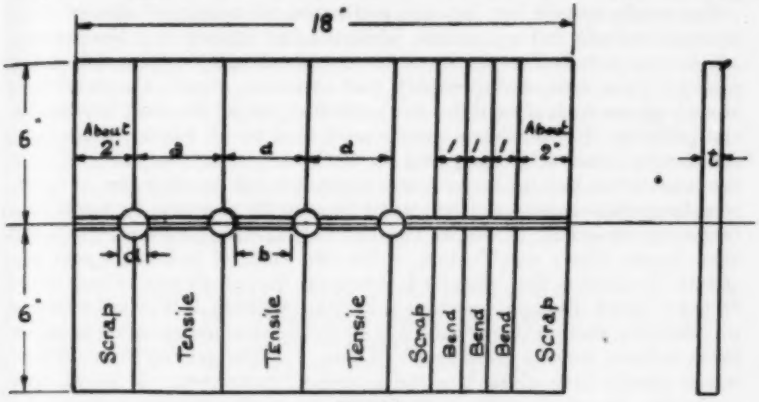

FIG. 19.

METHOD OF CUTTING-UP TEST PLATE
(DRAFT B.S.S. FOR ROUTINE TESTS FOR WELDERS).

welded joints, vertical, horizontal, overhead, etc., and at these he must practise assiduously until the instructor is completely satisfied as to his pupil's ability to be put on to simple production work. At this stage he must undergo a test to clinch the matter, two plates being welded together, and tensile test-pieces, including the joint, must show a weld strength of not less than 28 tons per sq. in., with satisfactory ductility, as shown by bend tests. The results of this test being successful, it can be said that he has advanced some considerable way towards his goal, although he must gain much further experience before he can be regarded as a fully skilled and competent welder.

COMPARISON OF METHODS OF TRAINING.

The above description of the boy's training is that received by him at a school attached to a number of works in this country, and will occupy at least two months, in many cases much longer. One must, however, consider also the Welding Schools of the Ministry of Labour, of which a number

have now been in operation for some years. In one of these schools, a six months' course is pursued, and the whole of the boy's time is devoted to welding, out of a week of 44 hours, about 2½ hours being spent on theoretical work and the balance in practical work. The instruction provided at these centres is undoubtedly of the utmost value. On leaving, however, the youth is at a disadvantage compared with the works-trained welder, in that he is completely unacquainted with the practice of the works which he is joining, and is consequently obliged possibly to unlearn some of what he has already learnt, and to learn a good deal that he might have been taught previously. Furthermore, the welding industry and the processes employed therein are in a state of continual flux, progress in welding equipment, for example, being so rapid that it is quite impossible for any full-time school to be or to remain completely up to date.

The works-trained boy has the additional advantage of always using modern methods and equipment, while the boy trained in a Government school may have had to obtain all his experience with equipment installed possibly some time, and probably now obsolete. Again, the conditions at such places must often differ markedly from those obtaining in commercial practice. He will have become used to a bench where his positions are always comfortable ones, and his work, etc., always adjusted to be of the correct height, and his previous experience will be therefore of correspondingly less assistance later, when he may be expected to work, as is frequently necessary, in confined spaces and exacting positions. It would thus appear that a combination of the two kinds of training would constitute the ideal. The difficulty is, however, that employers cannot afford to pay a youth during a possible six months' training, if they are receiving no return for their outlay; while it is obviously also unreasonable to expect them to train, for any great length of time, a welder coming from a school, which should have given him the necessary experience. It would seem preferable, therefore, to train the boy in the works, thereby ensuring his complete welding education in the same period. This could be achieved more cheaply than in the present Government schools—the products of which necessarily cannot be complete welders—by selecting certain first-class firms, and making them a grant for the boy during his instructional period.

Having thus satisfactorily trained the youth to the point when he can undertake simple jobs, an extremely capable supervisor is now necessary to take the welder slowly but surely on his way to become a skilled and reliable operator. He must not be taken along too rapidly, or he will be discouraged and his work will deteriorate; neither must it be too slow, or he will stagnate and become stale; much then depends on the ability of the supervisor to evaluate the abilities of his men so that they may maintain suitable progress. Nevertheless, be the supervisor as good as he may, his opinion of the ability of a welder should not be taken, unless supported by other evidence.

The necessity thus becomes apparent of devising some simple tests, which can be applied periodically, to ensure that the men are at least maintaining, if not improving, the quality of the welds they are laying down. Although some considerable amount of disagreement with the idea of testing welders has been apparent, it must at least be conceded

that it is better to ascertain the quality of the welds made by any operator by a test of some kind rather than by a failure in service; when, not only does the prestige of the firm suffer, but also the art of welding in general. To this end, therefore, the British Standards Institution have appointed a Sub-Committee to deal with the matter of a specification for the Testing of Welders, and have produced a draft specification under the title "Draft British Standard Specification for Routine Tests for Welders engaged in Metal Arc Welding." While certain modifications may be necessary, this appears to provide, at least, an admirable basis on which to work. The authors' firm has adopted these tests, and each quarter the welder prepares a test plate, 18 in. × 12 in., cut in the middle and welded together in accordance with the recommendations of the above specification. The plate thickness is $\frac{5}{8}$ in., the welds being ordinary butt welds of 60° angle, with no flats, the standard shop electrodes being used. Out of this plate are cut three tensile and three bend test-pieces, the size of the tensile test-piece being made smaller than that laid down in the proposed draft specification, for these required, to break them, a load greater than the maximum capacity of a 30-ton Buckton testing machine. The smaller test-pieces are $2\frac{1}{4}$ in. total width, with 1 in. drilled holes, giving an effective width of $1\frac{1}{4}$ in. The tensile strength of the three test-pieces thus made is calculated to tons per sq. in., the average figure being taken as representative of the work of the welder in question. The bend tests are evaluated according to the angle bent through, and whether any sign of cracking is apparent or not, as follows :—

Bent 180° O.K. = 33 (3 good bends = 100)
180° Insignificant crack = 30
180° Fairly bad crack = 25
180° Very bad crack = 22

For any other angle the value is found thus :

Say 80° (cracked) = $33\ \frac{80}{180}$ — deduction for crack.
= 14 — 1 = 13.

In addition, allowance is also made for the time taken for the job, the current consumed and the amount of electrode used. The results of typical tests, the first of three of such quarterly tests which have now been made, are shown in the Appendix to this paper, each man's results being reduced to a percentage by taking the best average tensile result as equivalent to 100 per cent.; whilst the lowest cost is equated to 100 per cent.; the lowest time taken to 100 per cent.; and the highest marks for bends to 100 per cent., the remainder being calculated to their respective percentages. The final column, the complete average value for each man, is obtained by adding four times the percentage under the heading : Quality of Weld (this characteristic being regarded as four times as important as any of the others) plus once the percentage under Cost of Weld, plus once the percentage under Time Taken, plus once the percentage under Bend Test, and dividing by 7. This method appears to give a very satisfactory Figure of Merit, which serves as a comparison in further tests.

As a result of these periodical tests, valuable information is obtained as to the welder's ability with respect to the class of work he is doing.

Should his work appear to be deteriorating, then a change of work is perhaps needed, or even a refresher course at the school may be advisable. The latter would, if possible to arrange, be of the greatest value, if taken occasionally, in keeping the welder thoroughly alive and up to date in his work.

The authors are indebted to the Directors of Messrs. W. H. Allen, Sons & Co., Ltd., for permission to present this paper. They are also under obligations to their colleagues, Messrs. T. H. Hall and J. Willey, for considerable help in preparing the paper, and Mr. J. R. Bryant, for the photomicrographs.

APPENDIX.

Typical Results of Tests on Welders.

Test plates have been prepared by four welders, in accordance with Draft British Standard Specification for Routine Tests for Welders engaged in Metal Arc-Welding, to determine their relative abilities to produce satisfactory welds for high-class work. The thickness of the plates was $\frac{5}{8}$ inch, and the welds were ordinary butt welds, 60° angle with no flats, Quasi Arc cellulose-covered electrodes being used in each case. The plates, after welding, were cut, not as laid down in the proposed specification—for these required to break the test-pieces a load greater than the maximum capacity of the tensile testing machine—but to give a smaller test-piece with which we could deal. The modified test-pieces were $2\frac{1}{4}$ inch total

Table I.

Tensile and Bend Tests.

Welder No.	Size of test-piece.			Actual load in tons.	Tensile strength tons per sq. in.	Bend.
	Width, ins.	Thickness, ins.	Cross-sect. Area, sq. ins.			
1	1·340	0·630	0·844	27·48	32·56	180° O.K.
	1·380	0·623	0·860	27·54	32·02	180° Insig. Cr.
	1·204	0·647	0·779	25·73	33·03	180° O.K.
					av. 32·54	
2	1·264	0·641	0·810	26·00	32·10	180° Insig. Cr.
	1·253	0·638	0·799	26·39	33·03	180° F.B. Cr.
	1·321	0·640	0·845	27·39	32·41	180° O.K.
					av. 32·51	
3	1·117	0·638	0·713	22·53	31·60	180° O.K.
	1·236	0·641	0·792	25·74	32·50	180° Insig. Cr.
	1·313	0·652	0·856	26·89	31·41	150° F.B. Cr.
					av. 31·84	
4	1·367	0·622	0·850	25·64	30·16	180° O.K.
	1·245	0·647	0·806	26·04	32·31	150° F.B. Cr.
	1·135	0·630	0·715	22·87	31·99	150° V.B. Cr.
					av. 31·49	

TABLE II.

Current and Electrode Costs.

No. 1: Current.

Average Volts 22 } ∴ Units cons. = $\frac{22 \cdot 183 \cdot 42}{1000 \cdot 60}$ kW./hrs. = 2·8 kW./hrs.
„ Amps. 183 }

∴ *Cost of Current* = 2·8*d.*

Electrodes. 3 ft. No. 8 size—cost is $\frac{12\frac{1}{2} \cdot 3 \cdot 12}{125}d.$ = 3·6*d.*

9 ft. No. 6 size—cost is $\frac{18 \cdot 9}{125}s.$ = 1*s.* 3½*d.*

3·5 ft. No. 4 size—cost is $\frac{22\frac{2}{3} \cdot 3 \cdot 5}{125}s.$ = 7½*d.*

∴ Cost of Electrodes = 2*s.* 2½*d.*

No. 2: Current.

Average Volts 24·5 } ∴ Units cons. = $\frac{24 \cdot 5 \cdot 200 \cdot 44}{1000 \cdot 60}$ kW./hrs. = 3·6 kW./hrs.
„ Amps. 200 }

∴ *Cost of Current* = 3·6*d.*

Electrodes. 3·5 ft. No. 8 size—cost is $\frac{25 \cdot 7 \cdot 12}{2 \cdot 2 \cdot 125}d.$ = 4·2*d.*

9·5 ft. No. 6 size—cost is $\frac{18 \cdot 19}{125 \cdot 2}s.$ = 1*s.* 4½*d.*

3·5 ft. No. 4 size—cost is $\frac{22\frac{2}{3} \cdot 3 \cdot 5}{125}s.$ = 7½*d.*

∴ Cost of Electrodes = 2*s.* 4*d.*

No. 3: Current.

Average Volts 25 } ∴ Units cons. = $\frac{25 \cdot 195 \cdot 44}{1000 \cdot 60}$ kW./hrs. = 3·6 kW./hrs.
„ Amps. 195 }

∴ *Cost of Current* = 3·6*d.*

Electrodes. 3 ft. No. 8 size—cost is 3·6*d.* (as above).

10·25 ft. No. 6 size—cost is $\frac{18 \cdot 10\frac{1}{4}}{125}s.$ = 1*s.* 6*d.*

3·5 ft. No. 4 size—cost is 7½*d.* (as above).

∴ Cost of Electrodes = 2*s.* 5*d.*

No. 4: Current.

Average Volts 23 } ∴ Units cons. = $\frac{23 \cdot 180 \cdot 43}{1000 \cdot 60}$ kW./hrs. = 3 kW./hrs.
„ Amps. 180 }

∴ *Cost of Current* = 3*d.*

Electrodes. 3·5 ft. No. 8 size—cost is 4·2*d.* (as above).

9·75 ft. No. 6 size—cost is $\frac{18 \cdot 39}{125 \cdot 4}s.$ = 1*s.* 5*d.*

4 ft. No. 4 size—cost is $\frac{22\frac{2}{3} \cdot 4}{125}s.$ = 9*d.*

∴ Cost of Electrodes = 2*s.* 6*d.*

width with 1 inch drilled holes. The tensile and bend results are given in Table I.

Current consumption and cost, electrode consumption and cost for each welder are given in Table II, whilst the times taken are given in Table III.

TABLE III.

Final Figures.

Welder's No.	Quality of weld.		Cost of weld.				Time taken.		Bend.		Final average. Percentage.
	Tensile strength tons/sq. in. Average of three results.	Expressed as a percentage.	Current. d.	Electrodes. d.	Total. d.	Expressed as a percentage.	Mins.	Expressed as a percentage.	Marks.	Expressed as a percentage.	
No. 1	32·54	100	2·8	26·5	29·3	100	42	100	96	100	100
No. 2	32·51	99·91	3·6	28	31·6	92·72	44	95·45	88	91·67	97·07
No. 3	31·84	97·85	3·6	29	32·6	89·88	44	95·45	82	85·42	94·59
No. 4	31·49	96·77	3	30	33	88·79	43	97·67	70	72·92	92·35

Table III gives the condensed results. The tensile results are reduced to a percentage, taking the best result as 100 per cent. Similarly, current and electrode costs are reduced to percentages, taking in each case, 100 per cent. as the lowest cost. Time taken was treated in the same way, the shortest time being regarded as 100 per cent. The bend tests were evaluated according to the type of bend given as follows :—

Bend. 180°. O.K. = 33 (three good bends = 100)
180°. Insignificant crack = 30
180°. Fairly bad crack = 25
180°. Very bad crack = 22

$$80°.\ \text{Cracked} = 33.\ \frac{80}{180} - \text{deduction for crack.}$$
$$= 14 - 1 = 13.$$

The final column, *i.e.* the complete average for each man, was obtained by taking four times the percentage under the heading Quality of weld, this characteristic being regarded as four times as important as the others, plus once the percentage under cost of weld, plus once the percentage under time taken, plus once the percentage under bend test, and dividing by 7 to give the final average.

The cost of the Quasi Arc electrodes were as follows :—

Size No. 8. 12*s.* 6*d.* per 100 electrodes
Size No. 6. 18*s.* ,, ,,
Size No. 4. 22*s.* 8*d.* ,, ,,
} all of 15-inch length each.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Sixty-ninth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, London, on Tuesday, February 11th, 1936. The President, Sir JOHN CADMAN, G.C.M.G., D.Sc., occupied the Chair at the beginning of the meeting, his place being subsequently taken by Mr. Ashley Carter (Vice-President).

The following papers were presented for discussion :—

"Welding Hard-Facings on Drilling Tools."
By J. Cuthill.*

"The Welding of Pressure Vessels."
By S. F. Dorey, D.Sc., M.Inst.C.E.†

"The Use of Welding in Transportation and Storage of Oil."
By A. C. Hartley, A.C.G.I., M.Inst.C.E., M.I.Mech.E. and A. C. Vivian, B.Sc., A.C.G.I., A.M.Inst.C.E.‡

"The Training of Electric Welders."
By W. G. Poole and R. T. Rolfe.§

A film of the construction of the Iraq pipe-line was also shown.

DISCUSSION.

THE CHAIRMAN (Mr. Ashley Carter) said he regarded the series of papers which had been presented as one of the most practical which the Institution had ever had.

It had been stated by Mr. Vivian that the cost of one particular type of joint was 10 per cent. and of another one 20 per cent. less than the coupled type, and he would like to know, taking those percentages of difference into account, how the actual cost of the welded type of each joint compared with, say, the coupled type of pipe to which reference had been made and on which the figures of 10 and 20 per cent. were based. He would also like to ask Dr. Dorey a question in connection with pressure vessels. Some of the welding referred to was of circumferential spiral form, and one weld shown was longitudinal. He would like to know the relative advantages of these two types of welds.

MR. A. FRANK DABELL asked Mr. Cuthill, with regard to his illustration of the method in which a bit was now built up, what length of bit was now being made as compared with the length of the previous type? If the present method of building up was carried out correctly and properly, he imagined the time had now arrived when bits could be made a certain length and maintained at that length by being built up.

DR. E. R. REDGROVE said that two types of welded joint had been shown. First of all there was the bell-mouthed, which he understood

* See pp. 205–210. † See pp. 211–223. ‡ See pp. 224–232. § See pp. 233–246.

had largely been replaced by the straight-butted type. He would like to ask whether the latter type of piping had been adopted not only because of its reduced cost, but also because it offered less friction to pumping, which he would imagine might be appreciable because of the little pockets left by the chilled sleeves. He also asked what method was adopted in the butt-welded joint, to prevent icicles dropping down into the pipe and impeding the flow?

Mr. W. H. Howe asked if it was not a fact that there was in England a great dearth of what were called, he believed, Class I welders, with the result that it was very difficult now to get delivery of fusion-welded plant? In spite of the good work that the big engineering firms were doing, was there not a lack of teaching of the higher form of engineering to which he referred? Possibly it was owing to the restrictions placed upon apprentices by the Trades Unions at the present time; but whatever the restrictions were, there was a limited supply of the super-welders who were so necessary, particularly in petroleum plant manufacture.

Mr. F. L. Bassett said he would like to hear something about the welding of thin sheet for the manufacture of drums; for example, lubricating oil drums, asphalt drums, and so forth. It was a question of resistance welding, and its merits or demerits as compared with arc welding, for anything, say, in the nature of 18 or 20 gauge sheet. Resistance welding had been generally used, but recently he understood that the arc process had been successfully established for sheet down to 22 gauge.

Mr. J. E. Willey said that Dr. Dorey had emphasized at the beginning of his paper that bare-wire electrodes were unsuitable for the welding of joints which required ductility, toughness and strength. Having had some experience in the early introduction of automatic welding in this country, he would like to ask Dr. Dorey whether the automatic welder shown in the illustrations was using bare wire, or if there was an automatic welder machine using covered wire at the present day.

Mr. J. V. Thomas, referring to Mr. Cuthill's paper and the use of the backing strip and tungsten carbide in welding, asked whether there was any preparation of the bit after the piece had been welded. Was there any grinding of the bit in any form, or was it left in the rough state as shown? He had personal experience of a tool steel which in the as-deposited state from the electrode was hard, so that it could be ground and a tool edge obtained. That steel was a tungsten–molybdenum alloy.

Mr. R. T. Rolfe said that Mr. Cuthill's paper took one back to the question of how the Egyptians used to cut their very hard stones, such as quartz and diorite, their methods being, he thought, fairly well understood at the present day. They used, for example, copper saws with large emery points fixed into them at intervals, and they probably drilled holes by using hollow copper drills fed with emery powder, a method which, incidentally, was used at the present day for the drilling of plate glass. The emery grains were more or less embedded in the soft copper, which was merely a carrier.

With regard to the question of the heat-treatment of pressure vessels dealt with by Dr. Dorey, one was faced with the fact that one could effect a complete release of stress by annealing at 600° C., and one obtained no further release of stress by annealing at 650° C. At 650° C., as was well known to the metallurgist, one was liable to destroy to some extent the duplex pearlite constituent, the ferrite of this being absorbed into the surrounding ferrite, and the lamellæ of cementite then spheroidized by reason of surface tension effects, the reinforcement which these "balled-up" particles of cementite afforded to the ferrite being considerably lower than in the case of the original unaltered pearlite, so that the mechanical quality was much poorer.

Again, normalizing at 900° C. effected no further release of stress than annealing at 600° C.; as shown by various tests made in their own practice. There was, however, one point of some importance in this connection: that, by annealing at 600° C., one would not correct any partial destruction of the pearlite which had been effected in the original welding. Here, there was a zone of intense temperature at the weld, and owing to the heat gradient extending from the weld, regions round the weld where the metal during welding was being annealed at 650° C., when spheroidization of the pearlite must take place to some extent. He had found that impact figure of 37 to 40 ft. lb. for the original steel might fall, owing to this effect, to 20 or 22 ft. lb. locally. By normalizing, one could restore this to the original figure, but by annealing at 600° C., one could not do so; while by annealing at 650° C., one might easily make matters worse. He did not know whether Dr. Dorey would consider that these considerations would make normalizing necessary as a final treatment. Normalizing would theoretically be preferable, but it would cost more, and the distortion might be somewhat greater.

Mr. E. A. Evans said that all the references made that evening, as far as he could see, had been to electric welding. Mr. Rolfe had shown some photographs of inclusions and, he thought, said that they were particularly prone to occur when bare wire was used. If that was so, was not one more likely to get inclusions with an electric arc than with an acetylene flame, because it is possible to obtain a better reducing atmosphere with acetylene than with an arc?

Mr. J. Cuthill, in replying to the discussion, said Mr. Dabell had asked if the application of hard-facings to fish-tail bits particularly had had any influence on the lengths required. He could not properly reply to that question, because he did not know what would have happened to fish-tail bits if hard-facing had not come into vogue. In the old days, fish-tail bits used to be called for in lengths of 30 inches and more. Sometimes the field staff added a few more inches to the length with a view to getting a longer life for each bit, but frequently drillers would have 6 inches or a foot cut off the blades in order to get the cutting edges nearer to the mud jets. Apart altogether from the question of hard-facing, it was quite likely that the lengths of fish-tail bits generally used would have been shorter. Nowadays they were generally called for about 24 inches long, from the shoulder to the cutting edge, and that seemed to be about the most economical length to start with.

With regard to the fish-tail bits which were built up as in the case of the last method he had illustrated, in which the whole edge of the bit and the old hard-facing were cut off by means of oxy-acetylene and the bit was then built up with a high carbon electrode in which the pellets of diamond substitute were embedded, no particular preparation was made other than grinding off roughnesses and excessive oxide by means of a hand grinding wheel. In some cases, after the building up of the new edge of the bit the whole blade of the bit was normalized. This normalizing was very advisable in this case, owing to the large body of welded material which in its initial state could only be considered a cast metal containing serious initial strains.

Dr. S. F. Dorey, in replying to the discussion on his paper, said mention had been made of the automatic welding machine and the use of bare wire. As a matter of fact, in ordinary work, *i.e.* tanks subject to no pressure at all or to very little pressure, the automatic welding was usually done with bare wire, the electrodes being either in coils or straight lengths and fed through the automatic welding head, which was controlled by a voltage relay connected across the arc. In the case of the high-pressure Class I welded vessels illustrated, covered electrodes were used. These were straight electrodes, 3, 6 or 8 feet in length, fed vertically downwards through the welding head. Arrangements were sometimes made for those lengths to be socketed one into the other, in order to ensure continuity of welding without breaking the arc. It would be appreciated that bare wire electrodes should not be used for this class of work.

Mention had been made of resistance welding in connection with very thin material. In that connection he might say that in America resistance welding had been developed to a considerable extent, and in this country certain firms were now making boiler tubes by the resistance welding process. In America, Lloyd's Register had approved of tubes for water-tube boilers made by the resistance method; they had been thoroughly tested, and found to be quite satisfactory. A considerable number were used in America, where the authorities seemed to be able to give more attention to welding than they did in this country, and viewed it more favourably. He might say that in this country fusion-welded boiler drums for marine work were not yet in use, whereas he thought that in America there must be about 600 drums in marine service. Some ships to be classed with Lloyd's Register were being built at the present time in America with water-tube boilers in which the drums were fusion-welded, each ship being fitted with three boilers. Manufacturers in America had made a very large number of welded pressure vessels, which had given satisfactory service for a number of years.

It was scarcely conducive to progress that certain inspecting authorities in this country were still apt to regard the welding of pressure vessels with a suspicion which was quite unjustifiable. This somewhat obstructive attitude precluded them from obtaining any experience of the application of welding to high-class pressure vessels. Fortunately Lloyd's Register were in a position to obtain experience in all parts of the world. There could be no question that a fusion-welded boiler drum made under expert supervision and exacting conditions of survey and testing was a

better proposition for high pressures than the riveted drum. In America the authorities recognized this fact and reaped the benefits accordingly.

Reference had been made to spiral and longitudinal welds. The spiral welds had been adopted by Messrs. Sulzer Bros., mainly, he thought, on account of the fact that the stresses in the welds were less when the welds were spiral than when they were longitudinal. The longitudinal weld took the full hoop tension in the drum shell. The Swiss Boiler Authorities evidently considered that the spiral weld was a type which they would be prepared to accept, and so the first drums were welded in this way. The tendency now was, for high-class work, to employ straight longitudinal welds. When Messrs. Sulzer Bros. first made spiral welds they had no X-ray apparatus, and no adequate heat-treating furnaces, which they had now.

Mention had been made of annealing at 600° and 650° C. and normalizing, in connection with the impact value in mild steel welds. Of course, the annealing at 600° C. was in the nature of a stress relieving treatment; it had no effect on the crystal structure of the material of the weld or of the plate. By increasing the temperature to 900° C. and slow cooling, a more uniform and refined structure throughout the weld and fusion zone would be obtained. Impact values were bound to vary according to the heat treatment carried out and, with a stress relieving treatment only, one expected to find different values in the weld to those obtained in the fusion zone and parent plate. The values may also differ in the weld itself, depending on the position of the notch, and having regard to the fact that deposited weld metal was not strictly homogeneous. The significance of impact values obtained from small specimens was a matter of some doubt, and he directed attention to the variation obtained on specimens cut from one piece of boiler-quality rolled plate. The rolling operation had a marked effect on impact resistance of small section specimens cut from the same plate, depending again on the position of the notch in relation to the direction of rolling. Invariably higher impact values were obtained on weld metal than on boiler-quality mild steel plate.

In regard to stress relieving temperature, he considered that 600° C. was sufficient to afford the required relief of stress in welded mild-steel structures. It was difficult to say exactly how much relief was actually obtained at this temperature. Stress relief was, after all, mainly a creep phenomenon. His experience showed that the figure indicated was entirely satisfactory assuming a high quality of deposited weld metal. Above 650° C. there was the danger of spheroidization, and he thought that with modern methods of temperature control in annealing furnaces there should be no difficulty in maintaining a temperature between 600° C. and 620° C.

Mr. A. C. Vivian, in reply, said on the question of the cost of pipe, the cost in the case of a 12-inch line of double-bell pipe was about 9 per cent. less than the cost of the screwed and socketed pipe per foot of length, and the cost of the plain-ended pipe, bevelled, was, roughly speaking, 20 per cent. less than the screwed and socketed pipe, per foot of length of pipe. The question that had been asked was as to the cost of making a screwed joint as compared with the cost of making a welded joint. There

was not a great deal of difference in cost; the welding was a little cheaper. But the point was that only one joint was made in 35 feet of length, on an average, and the cost of the joint was only a very small percentage of the cost per foot of the pipe-line. By devising a system whereby a cheaper pipe can be used, a very material saving is effected, and the overall cost of the whole length of line is very considerably reduced, not because one type of joint is cheaper to make than another, but because the cost of the pipe as a whole is reduced.

Reference has been made to a comparison between the belled-end joint and the straight joint, and the question had been raised as to whether the chill-ring in the double-bell joint introduced friction in pumping. It had been found that it did not do so to any extent, and it was in order to avoid any increase in friction in the line that the double-bell pipe had been devised. The inside diameter of the chill-ring was the same as the inside diameter of the pipe, and, although there might be a slight tendency towards eddies at the joint, it was not appreciable. He might mention in that connection that in the case of large gas lines the chill-ring was used, but without the pipes being belled, so that the inside diameter of the chill-ring was less than the inside diameter of the pipe-line, but it was found to be unimportant in the case of gas lines.

The reason why the double-belled end joint had been departed from and the plain end pipe was being used was simply a question of cost. Although it was necessary with the plain end pipe to run, say, three runs instead of two, the reduction in the cost of the pipe by the use of plain ends more than compensated for that.

With regard to the prevention of icicles, it had been found in practice that it was possible so to manipulate the arc that plain end pipes could be welded up without icicles being produced inside. The instance was given in the paper of an 8-inch line (which was something over 200 miles long) in which the pipe ends were set $\frac{1}{8}$ inch apart, having $\frac{1}{32}$-inch flats, and no difficulty occurred in the welding up of that line, because the welders were able to develop technique which ensured that the molten metal froze before it got completely through the pipe to form icicles.

Mr. W. G. Poole, in replying to the discussion, said that his firm had not suffered from a dearth of welders, possibly owing to the fact that they welded only for their own manufacture and not for the trade. They got youths who were suitable for the work, and that was a point of great importance. It was mentioned in the paper that welding consisted of doing the same thing over and over again, and for such work a certain psychology was required and it was necessary to get the right type of youth.

With regard to the advantages or disadvantages of oxy-acetylene welding as compared with electric arc welding, his firm had gone carefully into that question, and had come to the conclusion that they were equally satisfactory. The electric arc method was cheaper, but on the whole he thought each method had its uses. In Switzerland a great many aeroplane parts were acetylene welded, but in that case a thin material was being dealt with, and possibly for thin material oxy-acetylene welding was preferable.

THE CHAIRMAN, in proposing a hearty vote of thanks to the authors of the papers that had been presented, said he was sure everyone present would agree that those papers formed a most interesting series of contributions, covering the subject of welding in the oil industry from all points of view.

The motion was carried by acclamation and the meeting then terminated.

ANNUAL REPORT OF THE COUNCIL, 1935.

THE Twenty-Second Annual Report of the Council covering the activities of the Institution during 1935 is presented for the information of the members.

MEMBERSHIP.

The following Table shows the alterations in membership which have occurred during the year, and the total membership on December 31st, 1935:

	Total Dec. 31, 1934.	Changes during 1935.							Total Dec. 31, 1935.
		New.	Transferred to.	Resigned.	Deceased.	Removed.	Transferred from.	+ −	
Hon. Mems. .	22	—	—	—	1	—	—	− 1	21
Members .	610	38	10	13	7	3	—	+25	635
Assoc. Mems. .	478	34	12	6	1	13	10	+16	494
Students .	109	16	—	5	—	3	12	− 4	105
Associates .	87	7	—	2	—	2	—	+ 3	90
TOTALS .	1306	95	22	26	9	21	22	+39	1345

The corresponding increase of membership during 1934 was 56.

In addition to the above, on December 31st, 1935, 7 Members, 4 Associate Members, 3 Students and 1 Associate had been elected, but had not yet ratified their election, and 25 candidates were awaiting election.

The Council have to record with deep regret the deaths of the following members during 1935: Dr. David White (Honorary Member, Redwood Medallist, 1934), G. A. Buire, N. W. Graham, S. P. Harris, Lt.-Col. R. H. T. Jobson, Dr. A. D. Little, J. Towers, Dr. J. Versluys and K. Watts.

During the year Sir John Cadman, G.C.M.G., was invested by the Emir Abdullah of Transjordan with the title of Pasha, First Class, and by H.M. The King of Iraq with the Order of the Rafidain, First Class.

The third-class Order of the Rafidain was also bestowed on Mr. G. W. Dunkley, O.B.E., and the fourth-class Order on Mr. E. A. Satchell and Mr. W. E. D. Cole.

Mr. J. A. Jameson has been created Officier of the Legion d'Honneur.

Mr. F. G. Rappoport received the Order of "El Libertador" in the Class of Officer from the President of Venezuela.

ACCOUNTS.

The audited Accounts for the year ended December 31st, 1935, together with the Auditor's Report, are submitted.

A more detailed method of presentation has been adopted than in previous years. The principal items of expenditure have been grouped for convenient reference. The increasing annual income and expenditure

of the Institution warrants a change from the summarized form of Revenue Account adopted hitherto.

The Council have to report a substantial surplus of Income over Expenditure. This is mainly attributed to the increased membership and satisfactory sales of the Institution's publications.

During the year the Institution obtained recognition by the Commissioners of Inland Revenue as a "Charity" within the meaning of the Income Tax Acts. A repayment of Income Tax paid under Schedule D, or deducted from dividends at source, during the past seven years, amounting to £362 12*s.* 9*d.*, has been dealt with on the Balance Sheet and Research Fund Account.

A re-adjustment of investments has been carried out during the year. The holding of 3½ per cent. War Loan and 3½ per cent. Conversion Stock, being irredeemable stocks, were sold and the proceeds re-invested in three stocks having a definite redeemable date—3 per cent. Conversion Stock (1948–53), Manchester Corporation 3 per cent. Stock (1953) and Bristol Corporation 2¾ per cent. Stock (1955–65). A profit of £364 16*s.* 4*d.* was realized on the sale of the above investments, and has been re-invested as shown on the Balance Sheet.

The Council have authorized the formation of a Branch Fund, utilizing for the establishment of this fund the money refunded by the Iranian Branch in 1934. It is intended that this Fund shall be administered by the Council to further the activities of the Branches.

BENEVOLENT FUND.

The Audited Receipts and Payments Account of the Benevolent Fund for the year ended December 31st, 1935, are submitted.

The thanks of the Council are tendered to all members who have contributed to the Fund, and in particular to the members of the Trinidad, Iranian and South Wales Branches.

During the year the Benevolent Fund of the Institution also received recognition as a charitable body, and was able to obtain a refund of Income Tax paid during the years 1930–35 amounting to £16 3*s.* 6*d.*

The Committee of the Fund has been able to deal promptly with all necessitous cases which have arisen during the year.

The Council have authorized the publication of a separate booklet reviewing the work of the Benevolent Fund since its inception.

REPRESENTATION ON OTHER BODIES.

The Institution has been represented on the following bodies :—

The American Society for Testing Materials. *Dr. A. E. Dunstan and Mr. G. Sell.
The Advisory Board of the Department of Oil Engineering and Refining of the University of Birmingham. The President.
The British National Committee of the World Power Conference. Dr. A. E. Dunstan.
The Chemical Engineering Conference of the World Power Conference. Sir John Cadman, G.C.M.G. Lt.-Col. S. J. M. Auld, O.B.E., M.C., and Dr. A. E. Dunstan.
The Mechanization Board of the War Office. Dr. W. R. Ormandy.
The Ramsay Memorial Laboratory Advisory Committee. Mr. J. Kewley.

The Engine and Fuel Committee (joint Committee with the Institution of Automobile Engineers and the Diesel Users' Association). Dr. A. E. Dunstan, Mr. J. Kewley, Dr. F. H. Garner.

International Electrotechnical Commission. Mr. E. A. Evans.

International Drilling Congress (Paris). Mr. Ashley Carter.

British Standards Institution, Petroleum Industry Committee. Lt.-Col. S. J. M. Auld, O.B.E., M.C., Prof. J. S. S. Brame, C.B.E., Dr. A. E. Dunstan, Mr. E. A. Ellis, Dr. F. H. Garner, Mr. J. Kewley.

The Institution has also been represented on many other Committees and Panels of the British Standards Institution.

Second World Petroleum Congress, Organizing Committee. Dr. A. E. Dunstan, Mr. J. Kewley and the Secretary.

The Institution was consulted by H.M. Government in connection with the Regulations under the Petroleum (Production) Act 1934, and on the question of the Nomenclature of Petroleum Products.

MEETINGS OF THE INSTITUTION.

Eight General Meetings were held during the year, in addition to a Summer Meeting held on June 21st, 1935. A list of the Papers presented and their Authors is given below.

Date.	Subject.	Author.
Jan. 8th.	"Sulphur Compounds of Technical Interest. The Isomeric Thiophthens."	Prof. F. Challenger and J. B. Harrison.
	"Cold Tests for Fuels."	B. H. Moerbeek and A. C. van Beest.
Feb. 12th.	"Notes on the Petroleum Geology of Western Canada."	A. J. Goodman, Ph.D.
March 12th.	Annual General Meeting.	
April 9th.	"The Boundary Friction of Oxidized Lubricating Oils."	E. R. Redgrove, Ph.D., B.Sc., F.C.S.
May 14th.	"Viscosity and Thixotropy of Drilling Mud."	P. Evans and A. Reid.
Oct. 8th.	"The Costing of Petroleum Refinery Operations."	Gordon Kerr, M.A., C.A.
Nov. 12th.	Exhibition of Apparatus and Symposium of short papers.	Various.
Dec. 10th.	Symposium of papers on "Solvent Refining."	Various.
	Papers Presented at the Summer Meeting.	
June 21st.	Annual Reports on the Progress of Naphthology.	Various.

The Jubilee Banquet was held at the Park Lane Hotel on Friday, June 21st, and was attended by about 180 members and their ladies. The toast of "The Institution" was proposed by The Hon. R. G. Menzies, K.C., Attorney-General for Australia; Sir William Bragg, O.M., K.B.E., F.R.S., responded to the toast of "The Guests."

PUBLICATIONS.

The Journal.

Vol. XXI of the *Journal* was published in twelve monthly parts, and contained 19 Papers read at General Meetings of the Institution in London or at Meetings of the Branches, 31 contributed articles, the Annual Reports on the Progress of Naphthology and 1483 Abstracts of technical literature and Patents.

The changes in format and arrangement of the *Journal* introduced with Vol. XXI have been fully justified, and have been responsible not only for an improved appearance of the *Journal*, but also for a substantial reduction in the cost of production. The high standard of Papers and Contributions has been maintained.

Petroleum—Twenty-Five Years' Retrospect.

The Council authorized the publication in June 1935 of "Petroleum—Twenty-Five Years' Retrospect," commemorating the great advances in petroleum technology occurring during the twenty-five years' reign of His Majesty King George V.

The Silver Jubilee of His late Majesty coincided with the twenty-first anniversary of the foundation of the Institution. Congratulatory messages were received from The Secretary for Mines and the leaders of the oil industry in Europe and the United States. These messages formed an appropriate introduction to the reviews which followed, dealing with progress in every branch of the industry during the years 1910–35. The Council tender their thanks to all who contributed to this important publication.

The book was given to all members of the Institution in receipt of the *Journal*. It was very favourably reviewed in all quarters, and several hundreds of copies of the book have been subsequently sold to non-members.

Standard Methods for Testing Petroleum.

The third edition of "Standard Methods for Testing Petroleum and its Products" was published in June 1935. The various Sub-committees and Panels of the Chemical Standardization Committee had been engaged for some years on the revision of existing methods and the consideration of new tests, which were incorporated in the third edition.

The Council wish to express their appreciation of the extremely valuable work which has been carried out by these numerous Committees.

WORLD PETROLEUM CONGRESS.

An invitation was received during the year from the Association Française des Techniciens du Pétrole to hold the second World Petroleum Congress in Paris in June or July 1937. The Council were pleased to accept this invitation.

The task of organizing the second World Petroleum Congress will devolve on the French Association, but the Council is represented on their Organizing Committee, and will remain in close touch with the arrangements.

LIBRARY.

During the past year 372 books and periodicals were loaned to members as compared with 270 in 1934. A large number of inquiries were dealt with by personal visits, by correspondence and by telephone.

The resources of the Science Library have again been largely drawn upon, and members are reminded that books and periodicals available in the Science Library may be obtained on loan by application to the Librarian of the Institution.

AWARDS AND SCHOLARSHIPS.

The Students' Medal and Prize was awarded to Mr. H. T. Lorne, B.Sc., A.R.C.S., (R.S.M.), for his Paper on "The Adsorbent Action of Certain Natural and Treated Earths upon Bitumen and its Constituents."

The first award of the Students' Prize presented by Mr. T. C. J. Burgess has been made to Mr. B. O. Lisle for his Paper on "The History and Development of the Tankship."

The two Institution Scholarships, tenable at The University of Birmingham and the Royal School of Mines, have been awarded to Mr. C. S. Newey and Mr. R. O. Young, respectively.

RESEARCH FUND.

The Research Fund Committee has made grants during the year in assistance of the following investigations :—

"Steels for Use at High Temperatures"; to the British Electrical and Allied Industries Research Association.

"The Correlation of Redwood and Kinematic Viscosities"; to the National Physical Laboratory.

OFFICERS FOR SESSION 1936–37.

Sir John Cadman, G.C.M.G., Hon. LL.D., D.Sc., has been unanimously re-elected President for the Session 1936–37.

Lt.-Col. S. J. M. Auld, O.B.E., M.C., Mr. Ashley Carter, Mr. C. Dalley, Prof. A. W. Nash, Mr. J. McConnell Sanders and Dr. F. B. Thole have been elected Vice-Presidents.

BRANCHES AND STUDENTS' SECTION.

The Council are pleased to report that the Branches of the Institution in Rumania, Trinidad, Iran, Burma and South Wales continue in active progress, and are well supported by members of the Institution in those countries.

The Annual Reports of the Branches are printed below.

At the end of 1935 the Council approved the formation of a Branch of the Institution in the North of England. Considerable support has been promised for this Branch by members residing in the Lancashire and Cheshire area.

The London and Birmingham Branches of the Students' Section carried out very successful programmes of meetings and visits to works, of which details are given in the Reports printed below.

The Council desire to tender their thanks to the following for services rendered to the Institution: Lord Plender, G.B.E., Honorary Treasurer; Messrs. Ashurst, Morris, Crisp & Co., Honorary Solicitors; Messrs. Price, Waterhouse & Co., Auditors; and the Staff of the Institution.

The Auditors retire and, being eligible, offer themselves for re-election.

By Order of the Council,

ARTHUR W. EASTLAKE,

Honorary Secretary.

REVENUE ACCOUNT FOR THE

	£ s. d.	£ s. d.
To **Administration Expenses :—**		
Staff Salaries and Insurances	1412 17 4	
Printing and Stationery	192 19 3	
General Postages	186 5 0	
Telephone, Cables and Telegrams	23 3 3	
		1815 4 10
„ **Establishment Charges :—**		
Rent and Rates	450 4 4	
Cleaning and Lighting	75 6 1	
Repairs and Redecorations	74 9 1	
		599 19 6
„ **Publications :—**		
Journal Printing	1279 5 4	
Abstractors' Fees	219 11 7	
Postage on Journals	152 18 4	
Cost of Other Publications	598 1 3	
		2249 16 6
„ **Meetings, Hire of Hall, Preprints, Reporting, Etc.**		240 8 9
„ **Library Expenditure**		30 18 11
„ **Students' Scholarships and Prizes**		85 5 0
„ **Expenses of Students Section**		47 16 8
„ **Sundry Expenses**		138 16 11
„ **Depreciation of Office and Library Furniture and Library Books**		50 11 9
„ **Auditors' Fee**		42 0 0
„ **Balance, being Excess of Income over Expenditure for the Year, carried to Balance Sheet** ...		302 12 10
		£5603 11 8

RESEARCH FUND INCOME AND EXPENDITURE

1935.		£ s. d.
Jan. 1.	By **Balance brought forward**	351 3 9
Dec. 31.	„ **Income Tax** on Dividends for years 1928–34, now recovered	45 3 6
„	„ **Profit on Sale of Investments**	9 14 3
„	„ **Interest and Dividends**	10 2 2
		£416 3 8

YEAR ENDED 31ST DECEMBER, 1935.

	£ s. d.	£ s. d.
By **Subscriptions for 1935 Received During the Year :—**		
Members...	1833 4 8	
Associate Members	1110 15 0	
Students	93 9 0	
Associates	144 18 0	
	3182 6 8	
Special	20 0 0	3202 6 8
„ **Subscriptions in Arrear Received During Year...**		126 1 9
„ **Publications :—**		
Sale of surplus copies of Journal	1165 0 9	
Advertisements in Journal	380 10 9	
Sales of Other Publications	566 17 10	
		2112 9 4
„ **Interest and Dividends**		162 13 11
		£5603 11 8

ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1935.

1935.	£ s. d.
Dec. 31. To **Grants for Research**	54 11 0
„ „ **Balance carried forward**	361 12 8
	£416 3 8

BALANCE SHEET AS

	£ s. d.	£ s. d.	£ s. d.
Capital of the Institution under Bye-Law Section 6, paragraphs 14 and 15 :—			
Life Membership Fund—			
As at 31st December, 1934		624 0 0	
Entrance Fees—			
As at 31st December, 1934	2510 10 0		
Additions during year	136 10 0		
		2647 0 0	
Profit on Sale of Investments—			
As at 31st December, 1934	3 2 6		
Profit realized during year	323 9 10		
		326 12 4	
Donations—			
As at 31st December, 1934		326 5 0	
			3923 17 4
Students' Prize and Scholarship Fund :—			
As at 31st December, 1934		35 0 0	
Less : T. C. J. Burgess Prize awarded during year		10 0 0	
			25 0 0
Research Fund			361 12 8
Branch Fund (created 8th October, 1935) ...		150 0 0	
Less : Grants made for period ended 31st December, 1935		103 17 6	
			46 2 6
Members' Subscriptions Received in Advance			133 3 0
Journal Subscriptions Received in Advance			376 19 3
Sundry Creditors, General Account ...			158 17 11
Revenue Account :—			
Balance as at 31st December, 1934 ...		1094 13 7	
Income Tax on Dividends for the years 1928–34 now recovered		310 3 2	
Profit realized on sale of Investments held on account of Revenue		31 12 3	
		1436 9 0	
Add : Surplus for year as per separate statement		302 12 10	
		1739 1 10	
Less : Transferred to Branch Fund ...		150 0 0	
			1589 1 10
			£6614 14 6

AUDITORS'

We report to the Members of THE INSTITUTION OF PETROLEUM TECHNOLOGISTS and have obtained all the information and explanations we have required. We are correct view of the state of the Institution's affairs at 31st December, 1935, accordby the books of the Institution.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
31*st January*, 1936.

AT 31ST DECEMBER, 1935.

	£ s. d.	£ s. d.
Investment at Cost :—		
On Account of Capital :—		
£461 12 0 3% Conversion Stock	491 12 6	
664 6 6 London County Council 3% Consolidated Stock	481 10 6	
806 8 3 Manchester Corporation 3% Stock 1958	845 17 7	
867 8 6 Bristol Corporation 2¾% Redeemable Stock 1955/65	845 17 7	
100 0 0 Wigan Corporation 5% Redeemable Stock	99 14 11	
300 0 0 5% Conversion Stock 1944/64	336 4 6	
150 0 0 Wandsworth District Gas Co. 5% Debenture Stock	154 8 6	
400 0 0 Metropolitan Water Board "A" Stock 1963	346 10 7	
125 0 0 Great Western Railway Co. 5% Consolidated Preference Stock	105 4 9	
		3707 1 5
(Market Value at 31st December, 1935, £3933 6*s.* 8*d.*)		
On Account of Revenue :—		
£797 13*s.* 1*d.* 3% Conversion Stock	842 8 0	
On Account of Research Fund :—		
£336 5*s.* 10*d.* 3% Conversion Stock	357 14 8	
		1200 2 8
(Market Value at 31st December, 1935, £1187 14*s.* 1*d.*)		
Office and Library Furniture (excluding Presentations) :—		
As at 31st December, 1934	367 0 9	
Less : Depreciation...	36 14 1	
		330 6 8
Library Books (excluding Presentations) :—		
As at 31st December, 1934	55 10 3	
Less : Depreciation...	13 17 8	
		41 12 7
Members' Subscriptions in Arrears (not valued).		
Sundry Debtors and Payments in Advance :—		
Sundry Debtors, less reserve for doubtful accounts ...	178 11 9	
Payments in advance	30 11 6	
		209 3 3
Cash at Bank and in Hand		226 7 11
Cash on Deposit, General Account :—		
Chartered Bank of India, Australia and China	500 0 0	
Post Office Savings Bank	400 0 0	
		900 0 0
		£6614 14 6

Members of Council { JOHN CADMAN. / ALFRED C. ADAMS.

REPORT.

that we have examined the above Balance Sheet with the books of the Institution of opinion that such Balance Sheet is properly drawn up so as to exhibit a true and ing to the best of our information and the explanations given to us and as shown

PRICE, WATERHOUSE & Co.

BENEVOLENT FUND.

RECEIPTS AND PAYMENTS ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1935.

RECEIPTS.	£ s. d.	£ s. d.	PAYMENTS.	£ s. d.	£ s. d.
Balance at Bank on Current and Deposit Accounts, 1st January, 1935		750 6 6	**Grants in Aid**		175 0 0
Donations	42 16 8		**Loan**		10 0 0
Subscriptions	23 16 6		**Balance** at Bank and on Current and Deposit Accounts, 31st December, 1935		
Income Tax recovered	16 3 6		Specific Endowment Fund	170 0 8	
Interest	8 19 3		Benevolent Fund Account	487 1 9	
		91 15 11			657 2 5
		£842 2 5			£842 2 5

We have examined the above Receipts and Payments Account with the books and vouchers of the Fund and find it to be correct.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
3rd February, 1936.

PRICE, WATERHOUSE & Co.

TRINIDAD BRANCH.

REPORT OF THE COMMITTEE ON THE WORKING OF THE BRANCH DURING THE YEAR ENDED OCTOBER 31ST, 1935.

MR. G. H. SCOTT, B.Sc., resigned the Chairmanship at the end of the last session, and Commander H. V. Lavington, R.N., was elected in his stead. The Committee wishes to place on record its appreciation of Mr. Scott's work both as a member of Committee and as Chairman.

During the year five meetings were held, at which the following papers were read :—

Nov. 28th, 1934.—*Seventh Annual General Meeting.* "Gas Oil Separators," by J. W. Hardy, B.Sc., Assoc. Member.

Jan. 30th, 1935.—*Forty-First General Meeting.* "The Relationship of Mud to Electrical Coring," by H. C. H. Thomas, M.A., A.R.S.M., Assoc. Member.

Feb. 27th, 1935.—*Forty-Second General Meeting.* "Notes on Gum- and Colour-Stability Tests for Gasoline," by P. H. B. Trasler, B.A., Assoc. Member.

March 28th, 1935.—*Forty-Third General Meeting.* "Treatment of Water for Domestic Purposes on a Trinidad Oilfield," by A. H. Richard, B.Sc., A.C.G.I., A.M.Inst.C.E., Member.

April 24th, 1935.—*Forty-Fourth General Meeting.* "Notes on the Geology of South Trinidad with Special Reference to Palo Seco," by G. W. Halse, B.A., A.M.Inst.C.E., Member.

The average attendance of members and visitors was 27.

Early this year the Council acceded to the Committee's request for an increased grant in order to meet the growing expenditure of the Branch. From January 1st the quarterly grant of £6 was increased to £10.

Towards the end of last session a subscription list was opened to obtain funds to purchase a present for Mr. A. F. Dabell in appreciation of his services to the Branch as founder and first Chairman. Through the courtesy of the Kern Trinidad Oilfields, Ltd., a granddaughter clock was purchased in London, and the presentation was made by the President on behalf of the Branch at the Annual General Meeting this year.

The Fifth Annual Dinner was held on October 26th in Port of Spain, the Branch being again honoured by the presence of His Excellency, Sir Claud Hollis, G.C.M.G., C.B.E., who proposed the toast of the Institution. Ninety-six members and guests were present.

At the end of the year there were 62 members on the roll.

The audited accounts for the period under review are submitted.

It is with the greatest regret that the Committee records the death in October of Mr. Nelson W. Graham (Member).

The Committee wishes to extend the thanks of the Branch to Messrs. Middleton and Walsh, who again acted as Auditors, and to the Presidents and Members of the Apex and Point-a-Pierre Clubs for placing their rooms at the disposal of the Branch for its meetings.

H. V. LAVINGTON,
Chairman.

H. W. REID,
Hon. Secretary and Treasurer.

TRINIDAD BRANCH.

Accounts for Year Ending October 31st, 1935.

REVENUE ACCOUNT.

	$	$		$
To Stenographer's Remuneration		75.00	By Quarterly Grants from London	192.00
„ Printing, Postage, Cable and Sundries		21.00	„ Enrolment Fees	10.00
„ Loss on Fifth Annual Dinner		17.76	„ Subscription to Dabell Presentation	14.00
„ Draft on London, Benevolent Fund	123.45			
Less Subs. received	122.80			
		0.65		
„ Dabell Presentation—Purchase of Clock		37.84		
„ *Surplus for the year*		63.75		
		$216.00		$216.00

BALANCE SHEET.

Revenue Account:

	$		$
Surplus from last Account	47.75	Cash at Bank and in hand	111.22
Surplus from above Account	63.45	Sundry Debtors, per contra	10.00
	111.22		
Add Four Dinner Subs. outstanding	10.00		
	$121.22		$121.22

H. V. Lavington, Chairman.

H. W. Reid, Hon. Secretary and Treasurer.

F. Middleton, D. A. Walsh } Auditors.

BURMA BRANCH.

FIRST ANNUAL REPORT FOR THE YEAR ENDED DECEMBER 31ST, 1935.

FOUNDATION OF BRANCH.

A MEETING was convened by Mr. W. E. V. Abraham in the Volunteer Club, Yenangyaung, on January 24th, 1935, under the Chairmanship of Mr. G. W. Lepper, to discuss the desirability of forming a Burma Branch of the Institution. The meeting was attended by sixteen Members, Associate Members, Student Members, and Associates of the Institution, and by twenty-six non-members. Five Members who could not attend sent messages supporting the proposal to form a branch.

The non-members present unanimously welcomed the suggestion that a branch should be formed, and it was then decided unanimously to form a branch.

The following office-bearers and additional Committee Members were appointed by the members of the Institution, and were authorized to draft rules for submission to the Council :—

Chairman	Mr. G. W. LEPPER.
Deputy Chairman	Mr. W. E. V. ABRAHAM.
Hon. Sec. and Treasurer	Mr. C. E. KEEP.
Additional Members of Committee	Mr. T. J. F. ARMSTRONG.
	Mr. J. BENARD.
	Mr. E. J. BRADSHAW.
	Mr. G. COTTON.
	Mr. R. C. PARKER.

Of the above all were members of the Parent Institution except Mr. Bradshaw, who was elected from those Branch Members who were not members of the Institution.

The draft rules formulated by the Committee were submitted to and approved by the Council after minor amendments.

MEETINGS.

Four Ordinary General Meetings of the Branch and seven Committee Meetings have been held during the year.

The following papers have been delivered at the Ordinary General Meetings :—

February 2nd, 1935.	"Oil Winning," by W. E. V. Abraham.
March 22nd, 1935.	"Drilling and Fishing under Pressure at Masimpur, Assam," by P. Evans.
May 5th, 1935.	"Some Chemical and Physical Considerations Involved in the Cementing of Oil Wells," by A. Reid.
October 20th, 1935.	"Natural Gas Measurement," by F. E. J. Foxall-Smedley.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS, BURMA BRANCH.

FINANCIAL STATEMENT FOR THE YEAR 1935.

	Rs.	As.	P.		Rs.	As.	P.
To Subscriptions received from members for 1935	195	–	–	By *Expenditure* for the year :—			
„ Grants received from the Parent Institution for 1935 (Foundation Grant £5 and four quarterly grants of £6 each)	380	3	9	Hire of chairs and services of Police at Meetings	22	11	–
				Printing, typing, duplicating, stationery	18	6	–
				Purchase of nine notice boards	13	8	–
Suspense Account.				Postage	10	14	3
„ Subscriptions received from members for 1936	10	–	–	Cost of one Epidiascope	545	–	–
				Cash : with Honorary Secretary-Treasurer	70	–	9
Sundry Creditors.							
„ Cost of one Epidiascope advanced by the Parent Institution, £40 17*s.* 6*d.* at exch. 1/6	545	–	–	with Hong Kong and Shanghai Banking Corporation Ltd., Rangoon (as at January 29th, 1936)	449	11	9
Total Rs.	1130	3	9	Total Rs.	1130	3	9

C. E. KEEP,
Hon. Secretary-Treasurer.

We have checked and vouched the above statement and certify that it is correct:

W. A. DELAHAYE, A.C.A.
E. G. DUGGAN, F.C.I.S.

January 29th, 1936.

Membership.

At the close of the year the Branch had a membership of eighty-four, there being enrolled forty-one members of the Parent Institution, four intending members, and thirty-nine non-members.

Officiating Members of Committee.

The following members of the Branch have kindly officiated on the Committee during absences on leave of elected Committee Members :—

Dr. A. W. G. Bleeck, Messrs. H. C. Carter, D. C. P. Phelips, E. Procter, and A. Reid.

Mr. E. Procter also acted as Chairman during the absence of both Messrs. Lepper and Abraham.

Epidiascope.

Towards the end of the year the Branch purchased an Epidiascope at a cost of £40 17*s.* 6*d.*, this sum being advanced by the Parent Institution as a loan. Messrs. Burmah Oil Co., Limited, London, kindly accepted responsibility for transport and duty on the Epidiascope from London to Yenangyaung.

Financial Position.

The Financial Statement for the year is enclosed herewith. Rs.380/3/9 have been received from the Parent Institution, representing the Foundation Grant of £5 and the four quarterly grants of £6 each, while subscriptions from Branch Members for the year total Rs.195.

Cost of the Epidiascope amounts to Rs.545, at exchange 1*s.* 6*d.* to Re.1, while sundry expenses total Rs.65/7/3.

Cash in hand and at Bank at the end of the year amounts to Rs.519/12/6.

G. W. Lepper,
Chairman.

Yenangyaung,
January 30th, 1936.

RUMANIAN BRANCH.

THE Committee have pleasure in presenting the NINTH ANNUAL REPORT for the year ending January 31st, 1936, together with the accounts to that date.

Revenue Account for the Year ending January 31st, 1936.

Credit.	*Lei.*	Debit.	*Lei.*
Balance on hand at January 31st, 1935	1073	Expenses of Meetings	1750
DR. Balance at January 31st, 1935	2267	Postage	1150
		Printing	250
		Miscellaneous Expenses	190
	3340	Total	3340

The Branch register shows the following list of Members :—

Honorary Members	1
Members	32
Associate Members	14
Students	1
Total	48

which is an increase of one compared with a year ago.

The Eighth Annual Meeting was held on February 22nd, 1935, at which the chairman, Mr. Edeleanu, retired and was succeeded by Mr. Percy Clark. Also, two members of the Committee retired in rotation and offered themselves for re-election. No new nomination was received; therefore Captain Treacy and Mr. C. R. Young were re-elected without opposition.

Nine General Meetings were held during the year at which the following papers were read :—

February 22nd, 1935.	44th General Meeting. "Impressions of the Petroleum Industry in the United States," by N. Dragulanescu.
March 15th, 1935.	45th General Meeting. "Mechanized Stores Accounts," by J. Murray.
April 5th, 1935.	46th General Meeting. "Theory and Practice of Casing Programmes," by I. S. Rutherford.
May 14th, 1935.	47th General Meeting. "Synthetic Liquid Carburants," by Dr. E. Casimir.
May 24th, 1935.	48th General Meeting. "Present and Future Activities of Petroleum Syndicates," by A. Budurovici.
June 14th, 1935.	49th General Meeting. "Oil Occurrences in the Dacic in the East Gura Ocnitei Field," by R. P. Walters.
July 30th, 1935.	50th General Meeting. "The Killing of Well Craters by Controlled Directional Drilling," by H. J. Eastman.
October 4th, 1935.	51st General Meeting. "A Review of the Recent Advances in Petroleum Refining Processes," by D. I. Maxwell.
November 22nd, 1935.	52nd General Meeting. "Trends in the Manufacture and Use of Lubricating Oils," by O. A. Bell.

The Ninth Annual Dinner was held on December 7th, 1935, under the chairmanship of Mr. Percy Clark, and seventy-six Members and visitors were present.

Members of the Committee for the year were :—

Mr. P. R. CLARK, Chairman.
Mr. I. EDELEANU (ex-officio).
Mr. J. L. CHAILLET (ex-officio).
Capt. J. E. TREACY, Treasurer.
Mr. F. W. PENNY.
Mr. C. M. LEITCH.
Mr. E. C. MASTERSON.
Mr. C. R. YOUNG, Honorary Secretary.

The Committee again wish to record their thanks to the Chamber of Commerce, Ploesti, for the use of their hall for the meetings.

C. R. YOUNG,
Hon. Secretary.

SOUTH WALES BRANCH.

ANNUAL REPORT FOR YEAR ENDED 31ST DECEMBER, 1935.

MEMBERSHIP of the above Branch continues satisfactory, and attendance at meetings has maintained the high level set in the first session.

Six extremely interesting papers have been given during the Session. The average attendance has been between forty and fifty. On the occasion of Dr. Dunstan's recent lecture, thirty senior students from the University of Swansea were also present. In addition to our own meetings, members have had the privilege this year of attending meetings organized by other local scientific bodies, with whom we are working in close co-operation.

The Branch is indebted to Lieut.-Col. S. J. M. Auld, Mr. C. E. Spearing, Captain W. H. Cadman and Dr. A. E. Dunstan, who have come from London to address the Branch. Two papers were also given by our own members, Mr. E. Thornton and Mr. F. P. Alban.

We appreciate the interest shown by the Parent Institution, as instanced by the visit of the Secretary on the occasion of our meeting in December, 1935.

There is every prospect that the Branch, in its reconstituted form, will continue to prosper and to maintain interest in petroleum matters among a wide circle of people in the industry, as well as to arouse the interest of members of other scientific bodies not otherwise in touch with petroleum refining except as consumers.

The Accounts for the year ended 30th April, 1935, are appended.

W. C. MITCHELL, *Chairman.*
E. THORNTON, *Hon. Secretary.*

SOUTH WALES BRANCH.

Income and Expenditure Account for Year to April 30th, 1935.

EXPENDITURE.	£	s.	d.	INCOME.	£	s.	d.
To Epidiascope	58	11	3	By Members' subscriptions	10	2	6
,, Canteen charges for teas supplied prior to lectures.	7	7	3	,, Balance, being excess of Expenditure over Income, carried to Balance Sheet	57	6	0
,, Hire of Lantern		10	6				
,, Cheque book		2	0				
,, Stationery		17	6				
	£67	8	6		£67	8	6

Balance Sheet as at April 30th, 1935.

	£	s.	d.	£	s.	d.		£	s.	d.
Balance as at May 1st, 1934	84	15	6							
Deduct :—							Cash at Bank	27	9	6
Balance transferred from Income and Expenditure Account	57	6	0							
				27	9	6				
				£27	9	6		£27	9	6

IRANIAN BRANCH.

CHAIRMAN'S REPORT FOR 1935.

In my Report last year I lamented the fact that for some years the Local Branch of the I.P.T. had not been as active as the Parent Institution might have wished, but that a return to more healthy conditions of life was evident. It therefore gives me pleasure to record a continuance of this happy state of affairs, and my sincere wish is that the future career of the Branch will be as encouraging as it has been during the past year. There can be no doubt that the decision to prolong the existence of the Branch was justified, as the working of the past year amply demonstrates.

The past year's meetings have been well attended, and I believe much pleasure and profit have resulted from them. It is also gratifying to record that our colleagues in Masjid-i-Sulaiman have displayed a greater interest in our activities during the past year, and I trust we will do everything to stimulate their hearty co-operation in the future.

The finances of the Branch are in a healthy condition, due to the fact that our wants are few, and our operating expenses are therefore small. During the past season we have purchased an Epidiascope, and this should assist in making subsequent Lectures very instructive and entertaining.

During the season the following papers were read :—

(1) "Some Factors in the Design of Plant for High Temperatures and Pressures," by S. W. Adey, A.R.C.Sc., B.Sc., A.I.C.
(2) "The Deformation of Steels under Stress," by J. A. MacCash, B.Sc.(Eng.), A.M.I.E.S.
(3) "Welding Procedure and Control," by B. J. Brugge, B.Sc.
(4) "Commercial Progress," by G. H. Coxon.
(5) "The Scientific Control of Labour," by J. M. Moore, B.Sc.
(6) "The Rôle of Salt, Gypsum and Anhydrite in the Iranian Oil-fields," by P. T. Cox, B.Sc.

A talk by Mr. E. Thornton of Llandarcy on wax refining was also given.

The average attendance at the meetings was 80, which speaks well for the enthusiasm of the Members. The last three meetings were thrown open to the Abadan Staff.

The Membership of the Branch at date is as follows :—

Members	11
Associate Members	46
Student Members	10
Associates	5
Total	72

Five new nominations have gone forward to the Parent Institution during the year.

I wish again to place on record the thanks of your Committee and myself for the invaluable service of the Hon. Secretary, Mr. C. V. Rutherford. The revival of interest in the local Branch can be attributed in a large measure to the zeal and enthusiasm he displays in the Institution's affairs. Our appreciation is unreservedly offered to Mr. Rutherford for his whole-

INSTITUTION OF PETROLEUM TECHNOLOGISTS (IRANIAN BRANCH).

Income and Expenditure Account from January 1st to December 31st, 1935.

EXPENDITURE.	£	s.	d.	INCOME.	£	s.	d.
To Printing circulars, etc.	2	0	1	By Subscriptions	4	2	0
„ Postage		17	0	„ Excess Expenditure over Income	41	8	7
„ Epidiascope	40	11	6				
Payment to the Institution of Petroleum Technologists, London	2	2	0				
	£45	10	7		£45	10	7

Balance Sheet as at December 31st, 1935.

	£	s.	d.	£	s.	d.		£	s.	d.
Balance as at December 31st, 1934	71	19	2				Cash with A.-I.O. Co., Ltd.	30	10	7
Less : Excess expenditure over Income for the year 1935	41	8	7							
				30	10	7				
				£30	10	7		£30	10	7

hearted devotion to the cause, and I feel certain all the Members will join us in this. May I also be permitted to voice my grateful thanks to the Committee Members for their hearty support during the past Season. In conclusion, I trust the coming Season will be the best ever, and that all the Local Branches and the Parent Institution will touch a new high level of prosperity.

E. C. BREWSTER.
Chairman.

STUDENTS' SECTION (BIRMINGHAM BRANCH).

THIRTEENTH ANNUAL REPORT.

THE Committee has pleasure in presenting the Thirteenth Annual Report for the year ended December 31st, 1935.

At the Annual General Meeting the following officers for this Branch were elected.

Mr. P. A. TAYLOR (Chairman).
Mr. E. M. HOLBROOK (Vice-Chairman).
Mr. L. V. W. CLARK (Hon. Secretary and Treasurer).
Messrs. J. H. DOVE and D. SILVERTHORNE (Committee).

During the year six meetings were held and the following papers read :

January.	"Practical Applications of Geophysical Prospecting," by L. B. K. Happé.
February.	"The Uniontown Road Tests," by R. Stansfield.
March.	Annual General Meeting.
May.	"The Origin of Petroleum," by W. R. Wiggins.
December.	"The Design of Distillation Columns," by P. Docksey.
December.	"Fuel Oils," by A. H. Cowan.

The average attendances throughout the year were 18 members and visitors.

No visits were arranged during the year.

L. V. WOODHOUSE CLARK,
Hon. Secretary.

STUDENTS' SECTION (LONDON BRANCH).

TWELFTH ANNUAL REPORT.

DURING 1935 fourteen Student Members were elected. Three were transferred to Associate Members; eleven proceeded abroad and four resigned or were removed. The total Student Membership of the Branch on December 31st, 1935, was 54.

In order to enable junior employees of petroleum companies to participate in the activities of the Students' Section, the Council approved the admission of Associated Students to membership of the Branch. Rules governing the election of these Associated Students have been prepared and submitted to the Branch Committee for approval. Five Associated Students have been elected in accordance with these Rules and 4 are awaiting election, bringing the total of the available membership of the Branch up to 63.

At the Twelfth Annual General Meeting the following were elected to serve on the Committee: Messrs. Bridgwater, Boyd, Fasola, Ferguson, Haworth, Keach, de Mestre and Wright. Messrs. Bridgwater, Haworth and Ferguson were subsequently elected Chairman, Vice-Chairman and Hon. Secretary respectively. Mr. Haworth and Mr. de Mestre subsequently tendered their resignations on going abroad and Mr. Keach was elected as Vice-Chairman. The two vacant places on the Committee were filled by Messrs. Barrett and Groves.

The following twelve meetings and three visits were held during the year:—

January 10th, 1935.	Visit. Shell Laboratories, Fulham.
January 22nd, 1935.	Joint Meeting with I.A.E. Graduates' Section (London Branch). "The Lubrication of Automobile Engines," by O. T. Jones.
February 5th, 1935.	"Determination of the Cloud Point of Black Oils," by J. W. Hyde (Student).
February 12th, 1935.	Annual General Meeting. "Efficiency of Modern Distillation," by R. H. Keach (Student).
February 28th, 1935.	Visit. Gas Light & Coke Co., Beckton.
" " "	Annual Dinner.
March 8th, 1935.	Symposium. "Oil in Europe," by R.S.M. Students.
March 22nd, 1935.	"Health Hazards in the Petroleum Industry," by J. McConnell Sanders (Vice-President).
May 7th, 1935.	"Crooked Holes," by A. J. Haworth (Student).
June 3rd, 1935.	Second Annual Open Meeting. "Possible Improvements in Economy with Explosion Type Engines," by A. E. Chorlton.
October 14th, 1935.	"Value of Research in the Oil Industry," by Dr. A. E. Dunstan (Past President).
October 24th, 1935.	Visit. Messrs. George Kent Ltd., Luton.
November 5th, 1935.	"History and Development of the Tankship," by B. Orchard Lisle (Student).
November 19th, 1935.	Third Annual Open Meeting. "The Oil Industry and the World Crisis," by J. B. Aug. Kessler.
December 3rd, 1935.	"Action of Certain Natural and Treated Earths upon Bitumen and its Constituents," by H. T. Lorne (Student).
December 17th, 1935.	First of Series of Lectures on "Political and Economic Geography of Various Oil Producing Countries" (Burma, India and the East Indies), by Dr. L. Dudley Stamp (Member).

The general policy adopted during 1934 in respect of the Meetings and papers has been continued during the year under review. Three innovations were, however, made. It was decided that the Annual Open Meeting should be held in the early part of the Session in order that the greatest possible advantage should accrue from it. Secondly, a series of three lectures on the "Political and Economic Geography of Various Oil Producing Countries" was arranged with a view to providing a knowledge of these areas to Students who may later proceed abroad. Thirdly, a Joint Meeting was held with the Graduates' Section (London Branch) of the Institution of Automobile Engineers. This meeting was very well attended, and it was decided that, in view of its success, it should be made a permanent feature of the programmes of both Institutions. Contact has also been established with other Graduate and Students' Sections, as a result of which several invitations have been received by the Branch to participate in various meetings and social functions.

The visits arranged during the year have all been well attended and have proved very popular.

The attendance at the Meetings has shown some improvement, but as it has been somewhat spasmodic, the Committee still feels some concern. At the end of the Session the Committee will review the question of the type of paper presented, in order that as many as possible may be attracted to the Meetings.

In order to promote discussion, and also to assist the Committee to find likely authors of papers, a prize will be awarded at the end of the Session to the Student or Associated Student whose contributions to the discussions during the year are considered most meritorious by the Committee of the Branch.

The Committee would like to congratulate Mr. H. T. Lorne on being awarded the Students' Medal and Prize; Mr. B. O. Lisle on receiving the first award of the Burgess Prize; and Mr. R. O. Young on being awarded the R.S.M. Scholarship. The number of entries, however, for the two Prizes was rather disappointing and it is hoped that more Papers will be submitted next year.

The Annual Dinner, now firmly established as a popular feature of the year's activities, was well attended, and the Branch again had the pleasure of entertaining a number of guests, including several senior Members. The informal dinners held after the meetings have also been continued throughout the year, and have been generally well attended.

The Committee wishes to express its appreciation of the interest shown in the Branch by a number of senior Members; in particular by Mr. Ashley Carter, and other members of Council. It is hoped that during the coming year all Members of the Institution will make the activities of the Section known to their junior colleagues and staff, as the successful working of the Branch depends entirely on the measure of support received.

The executive officers would also like to thank Messrs. Astbury and Sell, and the other members of the Institution's Staff, for the considerable help which they have given and the useful suggestions which they have made.

B. C. FERGUSON,
Hon. Secretary.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

ANNUAL GENERAL MEETING.

THE Twenty-third Annual General Meeting of the Members of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C.2, on Tuesday, March 10th, 1936, at 5.30 p.m. The President, SIR JOHN CADMAN, G.C.M.G., D.Sc., occupied the Chair.

THE SECRETARY (Mr. S. J. Astbury) read the notice convening the meeting, the report of the Auditors, and the certificate of the Auditors to the Benevolent Fund account.

The Minutes of the Twenty-second Annual General Meeting, held on March 9th, 1935, were read and confirmed, and signed by the President.

THE SECRETARY announced that the following members of the Council had been elected as the result of the ballot :—

G. H. COXON.
F. H. GARNER, Ph.D., M.Sc., F.I.C.
J. S. JACKSON, B.Sc., A.I.C.
A. WADE, D.Sc., A.R.C.S.

It was agreed that the list of Members, Associate Members, Students and Associates elected or transferred between December 31st, 1934, and December 31st, 1935, should lie on the table.

THE PRESIDENT then proposed the adoption of the Annual Report of the Council for the year ended 31st December, 1935, and the Accounts and Balance Sheet at that date. Copies of the Annual Report had been circulated to all members of the Institution, and he assumed that it might be taken as read. (*Agreed.*)

The membership of the Institution was steadily increasing. During 1935 the net increase of membership was 3 per cent. of the total at the end of 1934. Ninety-five new members had been added to the Register during the year, but unfortunately losses of membership through death, resignation or removal amounted to 58. Nevertheless, the Council looked forward with confidence to a steady growth of membership.

It would be noticed that for the first time the Annual Reports of the Branches had been incorporated in the Report of the Council. As a result, members were provided with a much wider view of the activities of the Institution than was possible in the necessarily brief Report of the Council. If the total of all the members of the Institution who were members of one or other of the Branches was worked out, it was found to be 325—nearly a quarter of the total membership. To those must be added over 100 Branch members affiliated to the Burma, South Wales or

Northern Branches who were not yet members of the Institution. It must be a matter of considerable satisfaction not only to the Council, but to every member of the Institution, to know that the facilities of the Institution were in no measure confined to those members who worked in London. (" *Hear, hear.*")

He felt sure that all those present at the meeting would wish him, as President, to express, on behalf of the Council and the members, sincere congratulations to the Chairmen, Honorary Secretaries and Committees of all the Branches, on the records of a year's splendid work which they had accomplished, and he wished particularly to express thanks to Mr. Astbury for his valuable services. (" *Hear, hear* " *and Applause.*)

A fortnight ago he had had the privilege of inaugurating the new Northern Branch of the Institution. He had come away from Manchester greatly impressed with the keenness with which that most recent of the Branches of the Institution had been organized, a keenness which augured well for the future of the Branch.

He had said a moment ago that about one-quarter of the total membership of the Institution was provided with a local Branch. That, though a good beginning, still left much room for development. Although in some countries there was at present only a nucleus of members, he would like to assure them that the Council would give every encouragement and assistance to the formation of local Branches, wherever there existed a potential membership sufficient to warrant continued support to the Branch.

The type of meetings of the Institution most satisfactory to the members in London had received considerable attention from the Council. The attendances had shown distinct signs of falling off, and the highly specialized paper had not been proving attractive to the members. The Council came to the conclusion that a mixed type of programme would be most likely to meet the requirements of the London members. The inclusion of a paper on Costing, the exhibition of apparatus, and the two recent successful symposia of papers on Analytical Methods and Welding respectively had been steps in the right direction. A series of admirable papers on the geology and production of petroleum had been presented to the Trinidad, Rumanian and Burma Branches, and had subsequently been published in the *Journal* of the Institution.

Members had received a notification that the Second World Petroleum Congress was to be held in Paris in June, 1937. The work of the organization of that Congress devolved upon their French colleagues—the *Association Française des Techniciens du Pétrole*. The Council had given the Organizing Committee their fullest assurance of support, and he felt sure that the French Association would make every effort to ensure the Second Congress being a worthy successor of the First Congress.

He would like to say a few words about the Benevolent Fund. It would be seen from the accounts in the Report that the grants made during the year totalled £175. Of that total, £100 was a grant from a special fund which the Benevolent Fund Committee administered. The balance of £75, representing grants from the Benevolent Fund proper, was slightly more than the total of donations, subscriptions and interest received. The income tax recovered was a non-recurrent source of income. The net result was that the balance of the Benevolent Fund Account was slightly

less than it was twelve months ago. Fortunately the Benevolent Fund Committee had been able to deal promptly with applications for assistance as they had arisen. The calls on the Fund, however, were likely to increase as the membership of the Institution increased and as the passing years took their natural toll, and he would therefore appeal to all members of the Institution to give generously and regularly to their own Benevolent Fund, so that it could gradually be built up to dimensions commensurate with its needs, not only for the present, but also for the future.

Before calling on Mr. Adams to second the adoption of the Report and to deal more specifically with the Accounts, he wished to refer to one paragraph in the section dealing with the Accounts. It would be noticed that during the year the Institution, by virtue of its special aims and constitution, had been exempted from the payment of income tax. That meant that the Institution was recognized as a Society existing for the general advancement of knowledge, and not primarily for the personal interest of its component members. The exemption from income tax was a tangible recognition of the valuable work which the Institution was performing in furthering the scientific study of petroleum, and it laid upon the Council and the members an obligation to see that the high standard of their objectives was maintained. As a corollary, he felt that the time was coming when those objectives must be restated and when the constitution and structure of the Institution must be carefully examined. Only by rigorous self-criticism could the members be sure that the structure which had been built up in the first twenty-one years of the Institution's history was most suitably adapted and adaptable to the developments of the future. (*Applause.*)

Mr. Alfred C. Adams, in seconding the motion, said he would try very briefly to explain the salient points in the Accounts.

With regard to the Revenue Account, it would be noticed that it was presented in a more detailed form than had hitherto been the case. The revenue from the subscriptions paid by the various classes of members and also the revenue from publications were shown in detail, so that the members could see exactly what the figures were which related to each of the items. On the expenditure side of the Revenue Account, it would be found that the expenses had been grouped in a form which provided a more complete picture of the Institution's activities than had been shown in previous years. He was sure the members would agree that that method of grouping would very greatly facilitate comparison in future years. It would enable them to follow the comprehensive items of administration expenses, establishment charges and publications, and to see exactly what was the trend of events from time to time. It was difficult to make a ready comparison between the figures for 1935 and the corresponding figures for 1934, owing to the altered way in which they were now presented, but that difficulty would not be present next year. The three principal items of expenditure—administration expenses, establishment charges and publications—accounted for between 80 and 90 per cent. of the total expenditure during the year. The actual cost of the production of the *Journal* and other publications, without any allocation for salaries or establishment charges, was a little over 40 per cent. of the

total expenditure, but that item was nearly balanced by the revenue from publications, which would be seen on the other side of the Revenue Account. There was a difference between the two of about £130, which represented the final net cost to the Institution of the *Journal* and other publications, taking into consideration, of course, the sales of the *Journal* and the advertisements in it. That favourable position was due to the very satisfactory reception which had been accorded to some of the publications, including the third edition of "Standard Methods for Testing Petroleum and its Products" and the Institution's jubilee review: "Petroleum—Twenty-five Years' Retrospect."

The total receipts from subscriptions for 1935 received during the year amounted to £3202 6*s*. 8*d*. That did not include any credit for arrears of subscriptions, which were shown in the Balance Sheet as not valued at all. The corresponding income from subscriptions for the year 1934 was £3073, so that there was a satisfactory increase of £129 in the income from subscriptions. It was intended that in future all subscriptions in arrear which were thought to be of doubtful value but were recovered during another year would be shown as a separate item. The figure of £126 1*s*. 9*d*. shown in the Revenue Account as subscriptions in arrear received during the year represented amounts which had been written off in previous years as unlikely to be of good value.

The net result was that there was a credit balance, being excess of income over expenditure for the year, of £302 12*s*. 10*d*., which was carried to the Balance Sheet. (*Applause.*)

Turning to the Balance Sheet, he did not think there was very much in it which required explanation. It would be seen that the item of £302 12*s*. 10*d*. had been added to the Revenue Account, and there was also shown the amount of £310 3*s*. 2*d*. recovered from income tax, to which the President had referred in proposing the resolution. The profit realized on the sale of investments held on account of revenue was also shown. The members would understand that the first item of £3923 was the contra item for the investments shown on the other side, and the Balance Sheet showed £3707 as having been invested at the 31st December. A further sum of about £300 had been invested since then. All the Institution's investments were in Trustee stocks, and the members would see the very satisfactory market valuation which was shown in the Balance Sheet for their edification.

In view of the increasing activities of the Branches of the Institution, to which the President had referred in moving the resolution, the Council had decided that a special Branch Fund should be instituted to further the activities of the Branches. During 1934 a sum of £150 had been returned by the Iranian Branch, which represented grants made to that Branch in previous years in excess of its requirements. This amount was added to the revenue item which appeared in the Balance Sheet of 1934. The Council had decided to utilize that £150, and had taken it out of the revenue account and put it to the Branch Fund which had been created on the 8th October, 1935. It formed the nucleus of the Fund from which the requirements of the Branches were to be met. It would be seen that grants of £103 17*s*. 6*d*. had been made, which left a balance in the Branch Fund at the end of 1935 of £46 2*s*. 6*d*.

He did not think that the items in connection with the Research Fund and the Benevolent Fund required any explanation. The Research Fund had received some benefit from the income tax that had been recovered. He wished to endorse very heartily the President's remarks with regard to the Benevolent Fund, and he hoped that the members would pay due attention to them. The Council aimed at building up a larger capital fund for the Benevolent Fund of the Institution, so that eventually grants could be made not out of the capital, but out of the interest which the investments were producing. ("*Hear, hear.*") He thought that with a little patience and a little help and co-operation from the members the Benevolent Fund could be made a much more valuable feature of the Institution than it now was, and that was a very important matter, because there would undoubtedly be demands made upon the Fund in the future. He hoped that the Benevolent Fund of the Institution would become something of which all the members would be proud. ("*Hear, hear.*")

He felt that he had been able to present to the members a very satisfactory statement of the financial position of the Institution, and he had much pleasure in seconding the resolution proposed by the President.

The motion was then put to the meeting by the President and carried unanimously.

On the proposition of MR. A. P. CATHERALL, seconded by MR. C. DABELL, Messrs. Price, Waterhouse & Company were unanimously re-elected Auditors of the Institution at the usual fee.

THE PRESIDENT then moved that the By-Laws of the Institution be altered in accordance with the notice circulated to all members.

The motion was seconded by MR. J. MCCONNELL SANDERS, the Chairman of the Election Committee, which had dealt with the alteration in question.

The motion was carried unanimously.

THE PRESIDENT said he had hoped on behalf of the members to make a presentation to the Honorary Secretary, Mr. Arthur W. Eastlake, but unfortunately Mr. Eastlake was indisposed and was unable to attend. He had therefore written a letter to Mr. Eastlake, and had forwarded to him the sum of £100 which had been subscribed by the members as a mark of their appreciation of Mr. Eastlake's long service and the detailed work he had carried out in connection with the Institution. ("*Hear, hear*" *and Applause.*) It was over twenty-one years since the Institution had been founded, and in the work of its foundation Mr. Eastlake had taken the major part. The responsibility had devolved upon Sir Boverton Redwood as Chairman and Mr. Eastlake as Honorary Secretary. He had maintained his interest in the Institution ever since that time, and the little presentation which had just been made to him showed the appreciation which all the members felt, no matter in what part of the world they were living. In the letter which he had written to Mr. Eastlake he had expressed the best wishes of the members, and also their great regret

that Mr. Eastlake was not able to be present that evening to receive the presentation and to hear an expression of the appreciation of the members for his services. (" *Hear, hear* " *and Applause.*)

No other business being brought forward by the members, the meeting was thrown open to visitors, and THE PRESIDENT delivered his Presidential Address.*

MR. T. DEWHURST, in proposing a hearty vote of thanks to the President for his Address, said there was a very proper convention that the Presidential Address should not be the subject of discussion, but fortunately that did not prevent the members expressing their appreciation and thanks for the Address. (" *Hear, hear.*") He would stress the fact that the vote of thanks he now proposed was no mere conventional vote of thanks, for the Address which had just been delivered, delicately poised as it was between history and prophecy, was precisely what was needed at the moment to help matters forward in the right direction. He hoped he might be allowed to include in the resolution the thanks of the members to the President for the work he had done for the Institution during his past year of office. (*Applause.*) His manifold and heavy responsibilities in so many directions had increased the members' appreciation of the very large amount of work which he had been able to carry out for them. A year ago the Council, the members and friends of the Institution were delighted to learn that Sir John Cadman had accepted the Presidency, and their pleasure had recently been renewed on learning that he had accepted a further period of office. (" *Hear, hear.*") At the end of the present meeting Sir John would have established a record in the Presidential Chair. In all manner of ways he had given abundant manifestations of his interest in the welfare of the Institution, and it was therefore with the utmost confidence that he proposed the vote of thanks to Sir John and asked the members to confirm it by an expression of their approval.

The resolution was carried by acclamation.

THE PRESIDENT, in returning thanks, assured the members that the Institution would always receive his very active support. He realized the good work which was being done by the Institution and the important position it held in connection with the petroleum industry. That industry was moving rapidly, and what was common practice to-day was antiquated to-morrow. The members could not foretell what the future would bring forth, but they appreciated that the development of the industry demanded men of sterling quality and men who were fully equipped to carry on the activities of the industry, and it was to the Institution that the industry looked for leaders in that respect.

He thanked Mr. Dewhurst for his very kind remarks, and the members for the cordial way in which they had received his Address.

The meeting then terminated.

* See pp. 195–204.

CORRESPONDENCE.

To the Editor :—

SIR,

In reading the review of my monograph *Theorie und Technik des Crackens*, I cannot understand the reviewer's statement that "the book gives the impression of having been written at third or fourth hand." It must be admitted that, for the writing of scientific and technical books, all the literature on the subject must be referred to in order to give the reader a good general view. In preparing my monograph I followed the procedure, and in my opinion each source of information can be considered first hand, as it gives the opinions of experts regarding the subject treated.

The reviewer also "suspects," without any reason, that my description of the Dubbs process emanated from Dr. Egloff. I must protest against this unjust supposition, and suggest that, if the monograph is read more exactly, it will be found that this process is described according to my own experience, and that only the results of cracking Nienhagen crude are quoted from Dr. Egloff's article in *Petroleum*, No. 15, 1932.

My intention was to give a good view of the subject in a small space, and many authorities who have reviewed the work have found this to be fulfilled. Your reviewer has also stated that "the framework of the book is good enough, one half being devoted to the theory of cracking and the other to its practice; the sections are well chosen and taking them all in all, balanced in size."

Yours faithfully,

R. FUSSTEIG.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

The Eighth Annual General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on November 27th, 1935, Commander H. V. Lavington, R.N., Branch Chairman, in the Chair.

After the meeting the following paper was read by the Author :—

IMPROVED DRILLING SPEED AND ITS INFLUENCE ON COST.

By E. C. Scott, M.C., B.Sc. (Assoc. Member).

SYNOPSIS.

Recent improvements in machinery and methods have resulted in big increases in drilling speed in the United States of America, especially on the Gulf Coast.

These improvements have been brought about mainly by increasing the quantity of mud-flush circulated, through the use of big pumps operated by high-pressure boilers. The desire for increased fluid efficiency has also led to the use of drill pipe of larger diameter than previously, which in turn has dictated the use of very heavy hoisting equipment.

The application of these principles in a modified form in Trinidad is suggested, and it is maintained that the resultant increase in speed will yield a saving in drilling costs.

The writer has recently had the opportunity of witnessing the drilling operations on the Gulf Coast and in California, and of examining the equipment with which extraordinary drilling speeds are being achieved.

In this paper, therefore, it is proposed to examine firstly how these phenomenal speeds are obtained, and secondly, to discuss the actual intrinsic value of such operations, especially as regards the application of such methods to fields such as those of Trinidad.

On the Gulf Coast the highest speeds are attained at Bosco, Iowa and Baton Rouge. Bosco was instrumental in inaugurating this technique, and in the first place it was due to a California company adapting the methods of Kettleman Hills to the soft formations of Louisiana and Texas.

At Bosco an 8000 to 9000-feet well is being completed in less than a month. One well visited—Iseringhausen No. 1—had set 1200 feet of 13⅜-inch casing allowing 10 hours to set, had taken five cores from 7700 to 7900 feet and was drilling at 8300 feet on the twenty-first day after spudding in.

Another well at Baton Rouge had set conductor and drilled to 7300 feet in 11 days.

The one requirement to which all others are subservient is the maintenance of a large-volume flush system, composed of carefully prepared colloidal mud. Everything is done to achieve this. Very big pumps and high steam pressures are used; also large-diameter drill pipe with full-hole

tool joints and batteries of mud screens. Great care is taken to eliminate as much fluid friction as possible.

The handling of long strings of large-diameter drill pipe (up to 9000 feet of $5\frac{9}{16}$-inch is carried in some cases) calls for heavy hoisting machinery and powerful engines; therefore, the complete drilling rig is a very heavy and expensive outfit.

There is a very marked difference in equipment and methods used for drilling above and below the 6000 feet mark, when this is definitely a routine operation, and quite apart from the minor variations which were noted in the different fields having only a local significance.

A table of average sizes of equipment would read as follows:

Depth.	Dia. of drum shaft.	Engine.	Pump.	Capacity hoist gear.	Steam press.
Feet.	Inches.	Inches.	Inches.	Tons.	Lb./sq. in.
8,000–10,000 .	9″ –10″	14″ and 12″	$8\frac{1}{2}$″ × 20″	300	350
6,000– 8,000 .	$7\frac{1}{2}$″– 9″	12″	$7\frac{1}{2}$″ × 18″	150	300
4,000– 6,000 .	$6\frac{1}{2}$″– $7\frac{1}{2}$″	12″	$7\frac{1}{2}$″ × 18″	100	250
Not more than 4,000 .	$6\frac{1}{2}$″	12″ or 11″	$6\frac{1}{2}$″ × 18″ $7\frac{1}{2}$″ × 14″	60	200

The heavy rigs, 8-inch line shaft and above, use $1\frac{1}{4}$-inch wire line, and even rigs for use in 4000-feet territory are provided with efficient standby hoisting machinery.

Quite apart from insurance against mechanical breakdowns, it is maintained that such standbys save money in wire line, it being possible by their application to use 2500-feet lines, spool them tightly on the winding drum, and change their position on the sheaves continuously, thus obviating wear at one spot.

Draw-works.

There is a definite trend towards the "unit type" of draw-works, and many of the old jack-post type are being remodelled as such. Manganese-steel sprockets are not in favour, as it is claimed they lead to excessive chain wear. On the other hand, experiments are being made with machinery having machine-cut sprockets used in conjunction with precision chains, running in oil-baths, with dust-proof covers.

Opinion is divided on the subject of shaft and gear arrangements. The three-shaft set-up is universal, but some operators prefer that the line shaft be made light and serve only for cathead work, in which case only three speeds are used. This is the type mainly employed in conjunction with 350 lb. pressure steam. Others prefer the normal jack-shaft rig which carries four speeds.

So-called Hydromatic brakes are very extensively used for drilling in excess of 4000 to 5000 feet. It is only necessary to handle a brake lever of a draw-works equipped with one of these to appreciate the great saving in brake lining and drum-rim wear which results from their employment. They also decrease mechanical hazards and obviate much physical effort on the part of the driller.

Mechanical drilling controls are very little used nowadays. This is probably because the cost of electricity has risen to a point which makes its use too expensive.

Boilers.

In line with the desire for increased pump efficiency, boilers are being increased in working pressure; 250 lb. with 150° superheat is common, and many installations were seen using 350 lb. steam and 150° of superheat.

Superheaters are common, and were seen either fitted in the tubes of the boiler or as a separate unit.

The writer formed no definite opinion as to which of these types is the best. The separate unit is certainly more flexible, but is heavy and costs more to instal. Steam at high temperature will warp the slide valves of pumps and engines of older designs; therefore, where mixed equipment is used, the separate unit has much to recommend it, since auxiliary services can be run with saturated steam.

Boilers designed for 350 lb. steam are very heavy, and it is therefore common to see plants of five boilers of 123 h.p. each, whereas, in the case of 150 lb. steam, up to 175 h.p. boilers are used, in which case two or three are sufficient.

There is a noticeable trend to decrease the length of the tubes and increase the area of the firebox. This is more expensive in fuel, but it is maintained that on an oil-field this is of secondary importance, when compared with the advantages of quicker and more emphatic firing.

Most boiler plants are equipped with automatic devices to control firing and water supply. This enables the fireman to do a certain amount of rig work.

Engines.

Several 14 inch × 14 inch engines were seen, and also one or two 14 inch × 12 inch, but these are a very recent innovation, and are definitely much too heavy and expensive to be contemplated except for work in excess of 8000 feet. 12 inch × 12 inch engines form the vast majority of power units, and smaller ones are rarely used, even for drilling to less than 4000 feet.

One very interesting installation was a separate vertical 7 inch. × 7 inch twin steam engine for rotating the table, and direct-coupled to it through a 2 to 1 gear.

The writer is sure that more will be heard of this idea, as it clears the floor, decreases clutch, chain, sprocket and bearing wear on the rig, and saves steam and time. It also provides a means of turning the table if the main engine or transmission breaks down.

Electric and diesel drives are not common, and only offer advantages at locations remote from water and fuel supply.

The non-flexibility of the diesel engines introduces problems of drive which are not yet satisfactorily worked out. V-belts, and chains in conjunction with air-operated clutches, are being used, but all have their own particular disadvantages.

Pumps.

The emphasis placed on the efficiency of these was the most obvious note made. No detail is neglected to ensure their proper working. The units for cheap drilling are built so massively that one loses all sense of proportion in this matter. A pump as small as 14 inch × 7¼ inch × 14 inch is seldom seen. The vast majority of pumps are 14 inch × 7¼ inch × 18 inch, and there is a tendency to go to a 15¼ inch × 8½ inch × 20 inch size.

Plug-type valves, straight-line suctions, and large-diameter deliveries are used and, due to high steam pressures, compounding is not resorted to, except in cases of emergency. The side-by-side hook-up is almost universal.

Experiments are being made with a gear-driven pump operated by a direct-coupled reciprocating steam engine. It is claimed that by this method steam is more economically used and that wider pressure ranges are possible.

Hooks.

The design of casing hooks is still a very vexed question as far as very heavy design is concerned.

The Triplex hook is much used, but there is a certain antipathy to it in some quarters, due to its being constructed of cast steel.

Competitors to the Triplex hook have produced an instrument cut from solid steel with precision torch. This is, however, very expensive.

Swivels.

Big improvements in design are taking place in swivels, and roller bearings are being replaced by ball bearings efficiently lubricated by a circulating pump system driven by the rotation of the swivel itself.

Wash-pipe packings are now made to adjust themselves for wear by spring pressure, which saves a lot of cutting out of wash-pipe.

These were seen up to 300-ton capacity. The most common, however, ranged between 100 and 150 tons.

Crown and Travelling Blocks.

Design of blocks has not altered fundamentally. There are still two different types, depending on whether the combination rig with calf wheel or the standby draw-works is used. The former hook-up is fast decreasing in use for deep work, even in California, but it is here emphasized that for any work below 6000 feet some form of standby hoisting machine is always installed. A common practice is to rig up a standby drawworks below the derrick floor, using the side sill as a head-board. This is a comparatively cheap method, and avoids filling up the derrick floor-space.

Derricks and Substructures.

Derricks are mainly 136 feet high by 30 feet base, in order to handle three-collared doubles of 40 feet length.

Steel substructures and engine foundations are universal for exploitation work.

Many derricks have been increased from 122 to 136 feet by the addition of a rectangular or vertical section immediately under the water-table.

It is significant that even at Kettleman Hills, where unit control and considered conservative policy are the order of the day, drilling derricks are left standing in preparation for the pumping stage which is at least five years distant.

Foundations are always of concrete, and at deep wells are heavily reinforced with old sucker rods.

Cellars to accommodate massive master gate-valves and blow-out preventers have inclined step-ways down to them; but in California the derrick foundation is being increased in height to as much as 16 feet, in order to reduce cellar depth and also to provide an increased fluid pressure on the pump suctions.

Drill Pipe and Tool Joints.

Drill pipe is carried in $6\frac{5}{8}$-inch, $5\frac{9}{16}$-inch and $4\frac{1}{2}$-inch sizes. Very little drill pipe below $4\frac{1}{2}$ inch was seen, and for deep work the general policy is to employ the largest diameter drill pipe permissible, having regard to its tensile strength and the size of the hole being drilled.

The availability of heat-treated drill pipe (Grade D) has considerably increased the depths to which the larger sizes of drill pipe can be carried.

Tool joints are almost entirely of full-hole variety, and now that certain original weaknesses have been overcome, are entirely satisfactory. Tool joints are generally made up to drill pipe at the tool-joint factory.

Standards used for fitting tool joints at one factory are as follows:

Speed: 10 revs. per minute.

Torsion: Tong with a 2-feet lever exerts a 250 lb. gauge pressure on an 8-inch diameter pump cylinder.

Kellys.

These are generally 45 feet in length, of square cross-section, and have the tool joints machined on to the ends as an integral part, as opposed to screwing them on with a fine thread as heretofore.

Roller kelly bushings are very common, and would seem to be an economical fitting for deep work.

Drill Collars.

These are up to 40 feet in length, and it is becoming very common to make them without elevator necks. It is maintained that these are points of weakness, and since the running of a dog type overshot is never practised nowadays, their value as a fishing facility is negligible. All that is provided in their place is a series of riffles, such as are machined on rope sockets.

Bits.

Bit service in America is a very different proposition from what it is in Trinidad and other foreign fields. This is due to the fact that bit supply is run mainly on the hire system. Numerous firms are engaged in this business, and maintain service cars which travel round with bits and core barrels. These they leave at drilling rigs on the understanding that if they

are used, rent will be charged. Thus, small variations in conditions are catered for, and provided that the operator has a sound idea of what is required for a special condition, he can obtain it with great ease, and he is not worried with problems of repair and stock inflation.

As regards type of bit used, the fishtail in its original form has to all intents and purposes ceased to exist, and its place has been taken by two, three and four-winged bits, which resemble the ordinary soft-formation core head in shape, but are without the central core hole, and lack the pilot wings. In other words, when more than two wings are used, all are of the same dimension, and are symmetrically spaced on one plane round the bit body. These bits lend themselves to more accurate flush distribution, and are less weighty. They are the natural outcome of improvement in welding and in reamer design.

For harder formations there are many types of bit which embody grinding and crushing action in conjunction with the scraping action of the normal fishtail. These are definitely applicable to only very circumscribed conditions. They "ball up" in sticky shales, and will not face very hard rocks. An exaggerated appreciation of their value was very succinctly stated by one operator, who said to the writer that a bit, which was under discussion, was excellent for certain types of formation, but the trouble was, he did not believe that such formations existed.

Rock bits of both the roller and cone type are now built as separate entities of welded construction, independent of the body which carries the side reamers. They are called sport-type bits, but the name is in no way indicative of their nature. The cutters or cones run on roller bearings, which are welded into a cheap body, and when they are dull they are either returned to the maker or jettisoned. They are sold complete for about the same price as a set of replaceable cutters on the older models.

Mud Control.

Great attention is paid to accurate mud control. On the fields visited, normal drilling mud costs are heavy, quite apart from barytes expense, since very little colloidal material is produced during drilling.

Separation of sand and oil are the main problems, there being very little necessity to control high formation pressures by the addition of large quantities of weighting mineral. The heaviest mud the writer saw carried was 103 lb., at Lost Hills. This was used in conjunction with pressure equipment for drilling through a high-pressure water sand.

Operators in U.S.A. were generally astounded to hear that we carried mud up to 130 lb. per cubic foot in weight, and seemed to think that such mud would be too viscous to pump.

In line with the desire to promote the highest pump efficiency possible, great attention is paid to keeping mud in a fluid and sand-free state whilst maintaining in it a satisfactory colloid content.

Quebracho, soda and phosphate are used extensively to accomplish this.

Mud Treatment.

A vibrating screen is used on nearly every well, and where big pumps are used, as many as three are installed.

The Dorr thickener was seen on the Associated Oil Company's field at Ventura. This was a very costly and elaborate set-up for removing sand and oil. Such an installation would not be justified in Trinidad, where wells make such satisfactory native mud. In any case, the much less expensive centrifuge is performing satisfactorily at Ventura and elsewhere.

There is no doubt that in U.S.A. close attention to sand removal has greatly reduced the weight of mud which it is necessary to carry. This is specially the case in Kettleman Hills, where blow-outs no longer occur, in spite of the fact that mud weights have been reduced from 110 to 90 lb.

Pump Position.

Whilst every effort is made to ensure efficient pump operation, the methods of doing so vary considerably. Practice inevitably depends to a great extent on topography, and to a certain extent on the nature of mud treatment which is called for.

On the Gulf Coast, where the terrain is very flat, the old type slush pit is still used; but wherever the ground permits of drainage, the pumps are lowered to the level of the bottom of a mud tank. The flooded suction so obtained gives a very appreciable gain in efficiency and an economy in working parts, especially where mud is liable to become gas-cut.

One very interesting installation was seen at Kettleman Hills. Here, slush pumps and mud tanks are placed at the boiler plant and four wells drilled from one set-up.

This scheme has the following obvious advantages :—

1. Drier and higher pressure steam at the pumps.
2. Less cost per well installation.
3. Less boiler movement, since wells can be drilled at greater distances from a boiler plant.
4. Less storage and mud line movement.

In this installation an 8-inch victaulic mud line was provided for the returns, and this necessitated finding a boiler site at a lower level than any of the wells to be drilled. In Trinidad, where mud installations are so expensive to put in, this method should be tried, as suitable boiler locations are often easy to find. Remoteness of control of the pumps is not a serious objection, and it will probably pay to have a really good man in charge of these, who can use the boiler-man as an assistant.

Pump Hook-Up.

The pumps are nearly always placed side by side, and provision is made for a cross compound, which, however, is not used except as an emergency. Each pump is capable of circulating the well by itself.

A gear-driven pump similar to those used in conjunction with I.C. and electrical motors, but direct-coupled to a single-cylinder steam engine, is being installed at Kettleman Hills. It is hoped that this will effect a very large saving in steam, and by means of a simple alteration of gears will provide a bigger range of volume and pressure variations.

The idea has distinct possibilities, as such pumps can be hooked up to any form of power which circumstances dictate, and a standardized small engine which would do duty for turning the table, driving pumps, winding bailing drums and providing power for other temporary services, is a project which can be visualized as providing the solution to many present difficulties.

Straight-Hole Practice.

Straight hole is no longer the problem in America that it has been in the past in Trinidad. Good mud and pumps, combined with more accurate survey instruments and heavy stabilized drill collars, have accomplished so much that this subject is seldom alluded to.

The rapid strides made in directional drilling have also had their application in the maintenance of straight hole.

The extent to which the flush system is used to drill the hole undoubtedly assists in keeping it straight.

Stabilization is very important, and the insistence on so-called pendulum and gravity drilling is of secondary importance.

Whilst no more weight than necessary is ever carried, sufficient is applied to provide adequate penetration of the rock and to maintain a satisfactory rate of digging.

Many operators maintain that the acid bottle is not accurate enough, and that instruments reading to $\frac{1}{4}^\circ$ are necessary. Their experience is that it is easy to straighten a hole in which $\frac{1}{4}^\circ$ changes of inclination can be noted.

Opinion on the utilization of the three-point reamer is still far from unanimous, but objection to this form of tool comes mainly from the older type of operator.

The impunity with which the directional whipstock is run and fished out is very striking.

Speed of rotation is high, but there is a tendency to revert to a speed of about 90–110 revs. in place of 150, which was the practice until lately. This high rotary speed was very hard on equipment, and all but one of the major companies now consider it to be unnecessary.

Considerable importance is attached to maintaining balanced mud velocities inside and outside the drill pipe. This is done by selecting the latter in relation to the size of the hole being drilled, and is more particularly practised in sandy formations where there is danger in the settlement of cuttings.

Effect on Costs.

In America, the increase in speed has definitely saved money. Drilling contracts are now undertaken on the Gulf Coast for about $4.00 a foot down to 8000 feet. To this must be added three to four dollars a foot for casing and surface equipment, making a total of seven to eight dollars a foot, out of which presumably the contractor makes a profit.

The great effect which labour costs have is indicated by the following average cost of a well in the Oklahoma City field, drilled to the Wilcox sand, which occurs at 6500 feet.

Cost of Well Equipped for Natural Flow through Casing.[1]

(First Stage.)

Item.	Gross cost.	Salvage.	Net cost.
122-feet derrick with reinforcing legs	$4,675	$620	$4,055
Labour on derrick	825	—	825
Labour on cellar and pits	675	—	675
Drilling labour	65,833	—	65,833
Casing	29,755	—	29,755
Heavy well-head connections, clamps, valves, casing shoe, etc.	3,482	—	3,482
Cement	1,788	—	1,788
Labour, cementing casing	800	—	800
Company labour	1,500	—	1,500
Fuel, for drilling well	5,000	—	5,000
Water	860	—	860
Hauling	2,500	—	2,500
Incidental expense	1,000	—	1,000
Total natural flow well	$118,693	$620	$118,073

It will be seen here that at least 55 per cent. of the total cost is absorbed by labour, and that therefore any savings in time offer a big reduction in total cost on such fields in America.

In Trinidad the situation is very different, especially as regards the total cost of a well and the proportion of it attributable to labour.

Although the cost of a routine well in Trinidad varies considerably, dependent mainly on whether it is necessary to use barytes or not, the average can be said to cost from $20,000 to $30,000, and scarcely ever does a well cost more than $40,000.[2]

This amount can be analysed roughly as follows:—

	Per cent.
Casing	30
Other stores, inc. barytes	20
Tools and equipment	20
Steam, water and lubricants	10
Salaries and wages	20

This indicates that some 30 per cent. of the cost of a well is directly proportional to the time taken to drill it.

Thus let us suppose we are in a position to drill very expeditiously and complete a 4000-feet well for the minimum amount suggested above—$20,000; it will be seen that even at this admittedly low cost $1.50 per foot is controlled on the time basis, and that if we can double the rate of drilling, it is worth an expenditure of anything up to 75 cents per foot on equipment to do so.

It may seem optimistic to suggest that additional modern equipment will achieve such a result as this; but recent experiments in Trinidad have proved this to be indeed the case.

Whilst it follows that at the outset no very great monetary saving will be made, such increases in drilling speed, it is submitted, will pay for new equipment, and provide accuracy, dependability and quick results, which will eventually return handsome dividends.

The average rig in Trinidad drills from 1000 to 2000 feet per month, and therefore, if the foregoing contents are admitted, from $700 to $1,500 per rig per month can be allotted for purchases of machinery and tools.

Such a sum is outside the wildest dreams of most drilling superintendents, and it is obvious that great improvements can be made on much smaller budgets than this.

The Effect of Local Limitations.

Weight of Machinery.—Local roads and local weather conditions definitely limit the weight of machinery; but this is not a serious impediment to improving the performance of drilling machinery.

Drilling to more than 6000 feet is not yet routine practice in Trinidad, and until commercial oil is found at this depth, ultra-heavy machinery will not be necessary.

The heaviest portions of equipment are the boiler and the pump, and roads and bridges should in future be built to accommodate those up to a gross weight of 12 tons, as these are the mainspring of increased efficiency.

Testing Requirements.—The Trinidad oil-sand is so inconsistent in its occurrence that much coring and testing are often called for, and the desire for speed may lead to incomplete tests being made; therefore, in accelerating drilling, great care must be taken to provide for improvement in those directions.

Selection of Equipment to Provide Improved Results.—The following are the most obvious improvements that can be made in order of their importance:

1. Increased steam pressure.
2. Bigger pumps.
3. Better mud treatment.
4. Improved drill stems.
5. Improved testing and coring facilities.
6. Faster hoisting machinery.

Great stress has been laid on increased steam pressure—250 lb., or better, 350 lb. means the elimination of pump compounding, which is very costly, and the provision of increased slush volumes, which in turn produce straighter and faster hole with less bit-wear. Experiments are now being made to use steam more efficiently by driving the mud pumps with small engines through gears, and it is very probable that an attractive alternative to high steam pressure will soon be provided.

Bigger pumps for increasing flush volumes are scarcely less important than the steam required to operate them, and it is of very little use to buy big pumps and then operate them on low steam pressures.

The importance of mud treatment is generally appreciated, and has already been the subject of several papers read before the Institution.

Improved drill stems, such as heavy drill collars suitably stabilized, used in conjunction with drill pipe fitted with full-hole tool joints, permit more weight to be applied, and in this connection more accurate surveying instrument should be used. The acid bottle is good enough for holes destined for 4000 feet, but deeper holes should be more closely controlled.

Instruments such as wire-line core barrels and formation testers have not as yet been used in Trinidad, and a considerable amount of experiment will probably be necessary before they can be adapted to local conditions; such experiment should be persevered with, however, as great time savings and more accurate well information are visualised as a result of their employment.

Faster hoisting equipment is put last in order of importance, as it does not provide great savings unless much deeper drilling than at present is called for. On the other hand, the time lost in operating old and much-worn machinery is not generally appreciated.

The author wishes to thank Messrs. Trinidad Leaseholds, Ltd., for permission to read this paper.

References.

1 "Mechanical Equipment used in the Drilling and Production of Oil and Gas Wells in the Oklahoma City Field." Gustav Wade. U.S. Bureau of Mines Tech. Paper 561, 1934.

2 "Straight-Hole Technique in Trinidad and its Effect on Well Spacing," H. C. B. Hickling, *J.I.P.T.*, 1934, **20**, 936.

DISCUSSION.

MR. C. A. MOON quoted the Author's reference to Iseringhausen Well No. 1, where 1200 feet of 13⅜-inch casing was allowed 10 hours to set before they drilled ahead. He desired to know what cement was used, whether it was a specially prepared brand of cement or whether any reagent was used with the cement. If 10 hours were considered satisfactory in general in the States, then it seemed that in Trinidad they had to wait for an unduly long period.

He quite agreed with the Author's remarks about standby drawworks or some hoist on deep wells, so that 2500 feet of wire lines could be used to effect economy in wire lines; but he imagined that the chief economy over 1250 feet lengths was in the saving of labour in stringing up new lines, rather than in the wire lines themselves.

Reference was made by the Author to a 7 inch × 7 inch vertical twin engine used for driving the rotary table. It seemed to the speaker that it might be possible to use it in emergency for driving the draw-works, so that, if the main engine should break down, the unit might be used for pulling drill pipe out of the hole and running it back again while the main one was being worked over.

With regard to the Author's remarks about drill pipe and tool joints, he would like to know if there was any accepted depth at which a change from Grade "C" to Grade "D" was made.

Did the Author notice whether any demountable three-winged type of bits were a success? Were fishtails with the flush holes carried to the cutting edges used much, and was the wire line bit much in evidence?

MR. A. F. CASTLE said that he realized that a paper such as this was necessarily condensed, but he noticed that no mention had been made of the rotary hose. Presumably developments in this direction had kept pace with the rest of equipment. The all-steel hose had apparently

lost favour recently; but with the care which was taken to reduce the quantity of sand in the circulation, one of the main objections to its use, the tendency to cut out at joints, would have disappeared.

He would also like to know whether float valves were used to any extent in strings of drill pipe in the fields visited by the Author. With the use of the hydromatic brake, the float valve would be less useful. It had certain disadvantages, in that it caused the displacement of large quantities of mud when running in the hole, mud which was valuable and had to be accommodated. It also caused air to be trapped in the pipe when circulation was started, which caused the mud to be aerated and agitated, sometimes when it was least desirable. However, it had the advantage when drilling through pressure, as a certain amount of insurance in the event of failure of the hose or standpipe connections. It also reduced wear and tear on wire lines.

Mr. H. D. Fletcher referred to the statement that 55 per cent. of the cost of drilling in the U.S.A. was absorbed in labour, and that by utilizing heavier equipment and higher pump pressures and volume, a considerable saving was being effected.

By similarly increasing equipment in Trinidad a saving would no doubt be effected, but as labour costs are much lower here than in U.S.A., it would not be so great.

As a matter of fact, equipment on the Trinidad fields is being increased in power and speed as drilling becomes deeper, but, compared with the U.S.A., this change must necessarily be slow, for the reason that depths increase more gradually, and there is not the same amount of exploration drilling.

Supply houses naturally do their utmost to persuade operators to jump to the most up-to-date equipment, but the operator has to decide whether the expenditure involved is warrantable in his particular field.

He noticed in the last paragraph of the paper that the speed of the hoisting gear is put last in order of importance. He gathered from this that probably there is not much pulling out to change bits, and would like to know if the Author could say what footage is obtained before changing bits.

Lt.-Col. the Hon. H. C. B. Hickling said that the picture the Author drew of the Gulf Coast agreed with the usual description one heard given by drillers, that they " pumped it down."

He would like to know if the Author saw any cores there, and what was the toughness of the formation. Judging by the amount of flush that seemed necessary, their opinion would appear to be confirmed. It seemed that the coarse feed that could be taken there was very much greater than could normally be taken in Trinidad. Coarse feed would lead to coarse cuttings, and that necessitated a higher rising velocity, and so a larger volume of flush was required, and therefore larger pumps. The increase in the size of the drill pipe, of course, led to a decrease in the annulus and an increase in the rise of velocity, which was also along the same lines. In Trinidad they had occasional soft spots, and he could remember cases twelve or thirteen years ago where drillers made 300 feet a tour, and to-day they also found spots where that was possible; but on the whole he did

not think that the formation in Trinidad allowed of such coarse feeds, and where such coarse feeds could not be obtained, the necessity for such a volume of flush was non-existent.

He had always visualized increase in the speed of drilling as being divided into two sections. One was the time on bottom, and the other was the balance. Of course, an increase in speed going in and coming out did call for bigger hoisting gear, but, as the Author remarked, there was not so much to gain in that direction, but actually when one was on bottom and making hole, and one had arrived at the maximum feed that was possible whilst maintaining the verticality which was required, he thought it was necessary to design one's flush to suit the amount of cuttings that were to be removed. It had always been recognized good practice to get flush right down to the cutting edge of the bit, but he very much wanted to know how the Author considered that increase of flush made for increased verticality. He had very great difficulty in visualizing that. He could not remember seeing any instance where drill pipe could be placed on bottom and pumped down except in running into unconsolidated sand, where there was an explosive action going on and the sands were blowing up. He thought the whole object of the increased flush was to keep the hole clear of cuttings and prevent the bit from balling up.

He did not quite follow the remark that the cost of electricity made mechanical drilling controls too expensive, and would like to know why the cost of electricity would make mechanical control impossible.

He noticed that the rapid strides made with regard to directional drilling had also their application in the maintenance of straight hole. He therefore presumed that some of the holes had to be corrected. Reference to the survey instruments required to read as low as $\frac{1}{4}°$ would almost lead one to suppose that they started correcting holes when they were $\frac{1}{4}°$ off. Did that happen very frequently, or did they find it easy to keep within the limits they set up without directional drilling? There appeared to be very many methods of using directional drilling; one was to let your hole go off to somewhere near your target; another to make one big correction or make a correction when you were $\frac{1}{4}°$ off. That would necessitate a very accurate survey, and personally he scarcely visualized an instrument to give an accurate $\frac{1}{4}°$ reading. The other method would be to let the hole go off 2° or 3° and then correct; that would lead to a number of corrections of similar degree. In soft formation it was very much easier to maintain hole within the limits one required than it was when the ground was harder, and he suspected that the ease with which they obtained straight hole in the Gulf was due to the softness of the formation.

What was the time taken and cost of running a directional whipstock, not only the time taken by the rig in drilling past, but also the time spent in lining up the drill pipe? He supposed they needed a surveyor to mark the drill pipe, and each time the whipstock was used, the surveyor had to be brought back to put some more marks on the drill pipe.

He would like to know what exactly the contractors supplied for the prices paid to them. Did they provide their own steam, etc? That information was necessary in order to make any comparison with the costs quoted.

He agreed with the Author that the labour costs quoted for Oklahoma

were very high, and thought there must be a mistake. Assuming it was bare labour costs, and assuming that the driller got $15 a day and his crew $10, then it worked out roughly at over 330 days of 24 hours—that certainly seemed enormous. Of course, the price of that well worked out at $18 a foot, which was not very low, and even then, running through the items, he noticed there was no mention of overheads. Where exactly did those costs stop?

On the question of costs, he felt it was a great pity they had not some arrangement in Trinidad for uniformity in the costing of drilling. Unless the various items which were put into various costs were agreed, it was extraordinarily difficult to make any comparison. He believed that in the Rubber Industry in the Straits there was an organization, something similar to the Petroleum Association, and a uniform system of costing, and every company—values and circumstances being equal—found it quite easy to compare costs and put their finger on costs which were too high or extraordinarily low. It seemed that that might be worth while trying to bring about in Trinidad.

Later in the paper the Author mentioned the percentages applicable to the various heads of cost in Trinidad. There again, unless one knew what had gone into such heads, it was difficult to make comparisons. Was there any charge made for maintenance and depreciation? Such charges were absolutely necessary when one was trying to arrive at a fair charge for drilling equipment.

The method in which the Author had brought out the possible saving to be effected by cutting drilling time was very clear. But to arrive at such a saving one would have to accept that drilling time could be halved, and he fancied that was going to be rather difficult. Of course, every field could show a well here and there where the drilling time had been very short; what was required were averages over a long period, which must include all shut-down time, fishing time and every other time which might affect drilling plant charges.

Mr. R. Godfrey asked the Author if he saw or heard of any experiments carried out with multi-stage steam engines or pumps, because he thought that, with the degree of superheat mentioned in the paper, the ordinary engine and pump would be very inefficient.

Mr. A. J. Ruthven Murray congratulated the Author on his very interesting paper, and said he was sure they would all be interested to hear the Author's reply to Mr. Moon's first question in regard to the cementing of Iseringhausen No 1.

Concerning the use of 2500-feet wire lines, his Company had always used lines of that length, spooling the dead end of such line on a calf wheel. That method had been found so economical that he was surprised that other Trinidad operators did not do the same.

He quoted the Author's reference to the three-shaft set-up in drawworks, and referred to a four-speed one, of which he had had a specification recently, in which the line shaft only served as a cathead shaft, the four speeds being possible by virtue of a double chain driven from the engine to the

jack shaft, and inquired if the Author had seen any of them in use during his tour in the States.

On the question of steam pressures in relation to drilling speed, he said it was of interest to mention here, that on making a study of the drilling statistics over the past 12 months in four fields, he found that the footage drilled per day (actual drilling time not including time taken in rigging up) is as follows :—

Field No. 1 :
125 feet per day
Pumps—14 inches × 7¼ inches × 14 inches
Boiler Pressure—250 lb.

Field No. 2 :
115 feet per day
Pumps—14 inches × 7¼ inches × 14 inches
Boiler Pressure—225 lb.

Field No. 3 :
96 feet per day
Pumps—14 inches × 7¼ inches × 14 inches
Boiler Pressure—190–200 lb.

Field No. 4 :
78 feet per day
Pumps—12 inches × 6¾ inches × 14 inches
Boiler Pressure—140–150 lb.

He thought these figures showed how steam pressure had a very definite relation to the daily footage.

He would like to hear more about the automatic devices used to control firing and water supply at boiler plants.

With regard to bits, Mr. Ruthven Murray said he would be interested to know whether the three- and the four-blade bits were much in use for drilling through shale, and whether the four-blade was considered to be more stable, and therefore less likely to cause the hole to drill crooked.

He also desired to know whether in the soft formations of the Gulf Coast reamers were used of the type in which the cutter was set at an angle between the vertical and horizontal plane, or whether only of the type in which the cutter is mounted in the vertical plane. He wished to know this because some which he had seen advertised claimed to get better hole, due to a shearing action on the shale wall, whereas the other type was said merely to compress the shale wall by a knurling action, and this later permitted a reduction in the diameter of the hole due to squeezing-in.

He was rather surprised at Mr. Cooper Scott's statement that considerable amount of experiment would probably be necessary before wire line core barrels could be adapted to local conditions. He rather thought they were ideal for use in Trinidad, and that very little experimentation would be necessary. It surprised him that these had not been in regular use for years past, as they seemed to be such a valuable time-saver.

Dr. H. G. Kugler said that the extensive application of engineering principles during the last 15 years is undoubtedly responsible for the tremendous improvement in petroleum production practice so clearly demonstrated

by Mr. Scott in his valuable résumé of the latest innovations and developments.

The late depression in the oil industry was responsible for careful investigation into the application of economics without causing a final loss in revenues.

Improvements in methods for obtaining information on underground conditions is almost the first object a geologist would look for. He is not only entangled in the past, but sceptically looks into the future, fully realizing the obvious limits of economically exploitable oil deposits. He has to direct attention to, and prepare for, a time when oil will be more precious than now, and thus its recovery will become more lucrative.

Whatever change there will be in future production methods, the optimum results will only be obtained from accurate knowledge of the underground conditions. For such reasons a geologist attributes more importance to improved testing and coring facilties than rapid drilling. It was the speaker's opinion that in Trinidad, for instance, no oil-bearing beds over 100 feet in thickness should be passed through without a test of their content. The flow of oil relative to the size of choke, the gas/oil ratio, specific gravity and temperature of the oil, the reservoir pressure, etc., should be ascertained. With such knowledge at hand, one could calmly put all the tested reservoirs behind one string of completely cemented casing with the exception of the one to be produced first. The others could successively be tapped as the potential of the producing sand approaches that of a cased-off sand. Shot perforators will probably be of great value in such operations.

During the International Geological Congress, 1933, the speaker had the privilege to study the geological conditions of the Texas and Oklahoma fields. As far as the Tertiary beds are concerned, he could not observe a great difference in their hardness or texture when compared with those of Trinidad.

Mr. R. G. Perry said he noticed that Mr. Cooper Scott had mentioned that the fishtail type of bit had almost ceased to exist in the States, and that, through better practice in welding, a core-head type of bit had been evolved. He did not, however, mention it in his list of suggestions for improving local drilling, and it would be very interesting to know why he has omitted it.

Mr. G. H. Scott said that he considered Dr. Kugler had largely answered a question he was going to put to the Author, and that was the softness of the Gulf Coast formations in comparison with those of Trinidad. From general geological principles of similarity in age, depositional conditions and absence of secondary cementation, he should not imagine that there was any marked difference in the two series.

They had heard several remarks as to the adequacy of old drilling equipment and the economy of utilizing it rather than replacing it. Adequacy and the degree of obsolescence were largely matters of personal opinion.

It had been urged that the older rigs could be utilized for shallow wells. With depositional conditions as they were in Trinidad, and with the

extremely anomalous phases of oil accumulation, one could never definitely legislate for a shallow finishing depth at any location. In the speaker's opinion every rig should be able to proceed to the limits of the productive series at any location. It was, indeed, a very moot point whether all rigs should not be able to proceed beyond these proved limits until such operations were proved unprofitable.

The advisability of modernization could not, in his opinion, be decided merely on a cost-per-foot basis. Quite apart from the less tangible benefits of increased security, not only in the mechanical operations, but also to the personnel, in some cases profitability had to be taken into account. Thus a well might be stopped owing to the inadequacy of the plant in spite of the fact that deeper sands might exist. Thus the utilization of obsolescent plant can, in some cases, be the governing factor for the completion of a barren well or of a producer.

Mr. A. H. Richard agreed that a separate steam engine for rotating the table would clear the floor to the extent of replacing the rotary chain mounting by the drive shaft from the engine. But the engine being set on the floor, as he inferred, would cause more obstruction, and he requested the Author to give an explanation.

He could not see the importance of balancing velocities outside and inside the drill pipe. The criteria were a sufficiently high velocity in the annulus to carry the cuttings and as large an area as possible inside the drill pipe to reduce friction.

The trend seemed to be that straight hole was no longer a problem in America. They appeared not to have much trouble about it, and seldom alluded to the subject. It was, therefore, an extraordinary contradiction that they should have found it necessary to use more accurate surveying instruments reading to within $\frac{1}{4}°$.

He was inclined to think that the Author's statement that there was very little use in operating big pumps on low steam pressure rather an exaggeration.

Mr. E. C. Scott, in reply, said that so many questions had been asked and such interesting points raised, that it would take more time than was available to answer satisfactorily.

The paper covered such a broad field that it had been necessary to touch only lightly on each portion of the subject.

Mr. Moon had asked for information concerning the short cement setting times recorded. The Author did not know the specification of the cement used, but thought that it was one of the widely advertised special oil-well cements used extensively in the U.S.A. He did not know if any accelerator was used. The contention maintained was that the cement would set hard enough in 10–12 hours to permit of drilling proceeding, and it was assumed that the final hardening of the cement would not be interfered with.

He agreed with Mr. Moon that the 7 inch × 7 inch engine could be used as a hoisting stand-by, especially if some form of calf wheel were installed.

He thought that Grade D drill pipe was generally used below 6000 feet. The tensile strength of $4\frac{1}{2}$ inch Grade C was such that 9000 feet could be

safely used, but for the sake of safety in pulling on stuck pipe Grade D was preferred before this depth was reached.

Demountable three-winged bits were not much used, but one form of bit with wings, which were replaceable by a simple welding process, enjoyed a great deal of popularity.

He said that he agreed with Mr. Castle that the suitability of the steel hose was dependent to a certain extent on absence of attritive material in the mud. He had noted that more steel hoses were used on the Gulf Coast than in California, where the formations were relatively much more sandy.

With regard to the drill-pipe floats, these were extensively used; but at depth were carried comparatively high up in the drill stem. With a good non-viscous mud there was not much danger of gassing the mud.

In reply to Colonel Hickling, he said that he had seen cores of the Gulf formations, and thought that they were on the whole less sticky than the Trinidad Forest Series, but compared well with the Morne L'Enfer Sands and Silts.

He agreed that speeds attained on the Gulf Coast could not be imitated with economy in Trinidad; but he pointed out that big speed improvement was also being made in the hard rocks of California, and that it was Californian contractors who had adapted their methods to the softer formations of the Gulf Coast, and opened the eyes of operators there to the possibilities of the big rig.

He was afraid he had not made himself very clear on the subject of maintenance of straight hole. Accurate surveys were undoubtedly playing their part in indicating divergence from the vertical the moment it occurred. Stabilization of the drill stem was also important. Rectification of crooked hole with the whipstock was undertaken only in obstinate cases, but it was definitely a much quicker process than the holding up and reaming to straighten as practised in Trinidad. The survey of a hole and the setting of a whipstock did not take more than a day or two.

He said that it had been noted at Forest Reserve that the biggest tendency to deviate was in the Intermediate clay, which was presumably due to balling up of the bit. Both here and at Cruse, where balling up was prevalent, more efficient flushing had produced straighter and faster drilling.

The contractors in America provided all the drilling equipment, the steam and haulage. The owner paid for casing, cement and well-head fittings.

The Author agreed with Colonel Hickling that some form of standardized costing would be very helpful in arriving at comparisons of drilling and production costs. He foresaw great difficulty in introducing such a scheme, however, owing to the divergent nature of the accounting methods of various Companies.

With regard to Colonel Hickling's question as to whether any charge was made for maintenance and depreciation, the 20 per cent. for tools and equipment was considered to take care of this.

Colonel Hickling doubted the possibility of cutting the drilling time in half in Trinidad. Local circumstances and original speed were, the Author said, controlling factors; but, as stated in his paper, results of this nature were actually being achieved.

In reply to Mr. H. D. Fletcher, he said that he agreed with the contention

that one must certainly foresee sufficient deep drilling to justify the expense of improved machinery.

With regard to the faster winding speed being put last in the order of improvements, this applied to Trinidad, and not to the Gulf Coast, because in Trinidad roads, etc., necessitated a keeping down of weight.

Mr. G. H. Scott had introduced a very important point—namely, the inconstancy of the Trinidad oil-sand. The Author quite agreed that it was folly to rig up light machinery if there was the slightest doubt as to the presence of the shallow sand for which the well was intended. It was becoming very evident that a well could be drilled through the entire producing series without casing, and therefore it was important that key wells of this nature be drilled so that the most economical exploitation programme could be formulated.

Mr. R. Godfrey had asked if any double- or triple-expansion engines were being used. The Author said in reply that he had not seen any, and assumed that these would be much too cumbersome.

In reply to Mr. R. G. Perry, he said that he had not stressed the advantages of improved forms of bits because in the past specialized forms of bit had not been too successful in Trinidad. The situation might alter considerably in the near future, but in the meantime there was no justification for assuming an improvement.

In reply to Mr. A. H. Richard, he said that when a calf wheel is used as stand-by, the auxiliary engine is placed ahead of the driller; *i.e.*, the table is turned 90 degrees from its normal position. This cleared the floor of the rotary chain and its guard and gave much more room, especially if racking in front of the drum is practised. He agreed with Mr. Richard that the term "balance of velocities" was an unsatisfactory one.

With regard to the use of big pumps with low steam pressure, he said that the design of the modern pump was such that it would not work well on small steam pressures.

In reply to Dr. H. G. Kugler, he said that he quite admitted the danger of stressing the speed factor to the exclusion of all other interests.

Improvement in drilling should certainly provide for more complete testing and better finishing practice. Such improvements were being made at comparatively little sacrifice of speed, and it should not be forgotten that if the top rocks, which were of little interest to the geologist, could be drilled more quickly, more time would be available for proceeding with caution in the oil-sand zones.

In reply to Mr. A. J. Ruthven Murray, he agreed that the calf wheel was an economic fitting for medium depth wells, and thought that their use was to be recommended, especially if they were available from field stocks. A stand-by draw-works is preferable, however, as it can be used to pull out of the hole, and further permits of the line being wrapped tightly on the drum.

With regard to the number of wings used on a bit, the matter was generally to be decided by trial. Too many wings would cause balling up in soft formations, whereas in hard formations the abrasion of the cutting edges was distributed over as many wings as possible to avoid increasing the number of round trips.

Answering Mr. Murray's question on the action of vertical and inclined

reamer rollers, the Author thought that this was again a question of suitability to the rocks being drilled. When only stabilization was required, it had been found that smooth reamer rollers were very efficient.

On the Chairman's proposal a very hearty vote of thanks was accorded the Author for his paper, and the President and Members of the Apex Club for the use of their rooms.

Mr. A. H. Richard, in a written contribution, noted from the Author's reply that the particular reference to bigger pumps was intended to mean bigger pumps designed to work at higher steam pressures.

Lt.-Col. the Hon. H. C. B. Hickling, in a written contribution, said Mr. Scott states in the paper that in the fields visited by him it was considered that "stabilization is very important and the insistence on so-called pendulum and gravity drilling is of secondary importance."

During the discussion, Mr. Scott, in answer to questions, stated that instruments to read $\frac{1}{4}°$ of deflection were considered necessary, because operators stated that whilst a deflection of $\frac{1}{4}°$ could be easily corrected, a deflection of 1° was very much more difficult to deal with.

Mr. Scott stated that the method used to correct such deflections was to rotate rapidly (presumably at one spot or with a very fixed feed) until verticality was obtained.

Whilst a well is being drilled with stabilized drill collars and is being maintained truly vertical, it is obvious that gravity and/or stabilizer may claim to share the credit, but when such a hole is deflected and is then corrected by the above method, it is difficult to allow any credit to the stabilizer.

In such cases gravity and its horizontal component tending to bring a deflected string back to the vertical is the only force available, and should be allowed the credit.

For a stabilizer, having once drilled round a corner, will always follow the same line, and in certain cases will actually slow down any process for correction.

Mr. E. C. Scott, in reply to Colonel Hickling's written contribution, said the contention that once a hole is crooked that only gravity can bring it back to the vertical is correct.

Reamers or stabilizers tend to minimize the cumulative effect of an inclined hole which is caused by sag in the drill pipe. It is this sag in the drill pipe which makes it so difficult to straighten in the inclined portion of a hole. Incidentally, positioning of a reamer just above the point of first flexure will very often straighten the hole very quickly, especially where a big hole is being drilled.

THE RELATIONSHIP BETWEEN THE CONSTITUTION AND VISCOSITY CHARACTERISTICS OF HYDROCARBONS.*

By W. R. Wiggins, B.Sc.

The synthesis of hydrocarbons of the lubricating-oil range is the subject of research now being carried out. From a study of the physical properties of these hydrocarbons it is hoped to determine those types which are likely to be present in petroleum lubricating oils, and, further, to indicate those hydrocarbons which from their physical and chemical properties are most suitable for the purposes of lubrication.

Viscosity and viscosity–temperature stability † are physical properties of primary importance for lubricating oils. As a preliminary step, therefore, it was decided to correlate available data on the influence of constitution upon viscosity and viscosity–temperature stability for the simpler hydrocarbons, and to investigate the application of the resulting generalizations to the higher lubricating-oil hydrocarbons.

The constitution of a hydrocarbon is reflected to a varying degree by its physical properties. Density, boiling point, viscosity and viscosity–temperature stability, for example, are not entirely additive, but depend to a considerable extent on chemical structure. It is known that with hydrocarbons of the same class or type the density, boiling point and viscosity increase with increase of molecular weight, but this does not hold when the corresponding hydrocarbons of different chemical classes are compared. The presence of aliphatic straight-chain or branched-chain structure, of unsaturation, or of aromatic or naphthenic rings, has a specific effect upon the physical properties.

Paraffin Hydrocarbons.

Paraffin hydrocarbons have relatively low densities and viscosities. The variation in viscosity of the normal paraffins with temperature is comparatively small, and at the boiling point all paraffins approach the same viscosity. Table I ‡ shows the variation of density and viscosity with increase in temperature.

Fig. 1 shows how the viscosity of the normal paraffins increases with increase in the number of carbon atoms. The logarithm of the viscosity at 20° C. has been plotted against the number of carbon atoms in the paraffin molecule, and a straight-line relationship is obtained. An abnormality occurs from the eleventh to the thirteenth carbon atom, and this is in accordance with the helical structure of the molecule postulated

* Paper received February 11th, 1936.

† Viscosity–temperature stability is a term used in this paper in preference to temperature coefficient of viscosity. A high viscosity–temperature stability corresponds to a low temperature coefficient of viscosity.

‡ The data given in the succeeding tables are taken from the International Critical Tables, unless otherwise stated.

TABLE I.

Hydrocarbon.	Density at			Viscosity in centipoises at					
	0° C.	15° C.	20° C.	0° C.	20° C.	30° C.	40° C.	60° C.	80° C.
n-Pentane . .	0·645	—	0·631	0·283	0·232	0·212	—	—	—
n-Hexane . .	0·677	—	0·660	0·396	0·320	0·290	0·264	0·221	—
n-Heptane . .	—	0·688	0·684	0·519	0·410	0·369	0·334	0·276	0·232
n-Octane . .	—	0·706	—	0·703	0·538	0·478	0·428	0·350	0·290
n-Nonane . .	—	0·722	0·718	—	0·624	(22·3°)	—	—	—
n-Decane . .	—	—	0·747	—	0·78	(22·3°)	—	—	—
n-Undecane .	—	—	0·741	—	0·94	(22·7°)	—	—	—
n-Dodecane .	—	—	0·768	—	1·15	(23·3°)	—	—	—
n-Tridecane .	—	—	0·757	—	1·52	(23·3°)	—	—	—
n-Tetradecane .	—	—	0·765	—	2·22	(21·9°)	—	—	—
n-Pentadecane .	—	—	0·772	—	2·86	(22°)	—	—	—
n-Hexadecane .	—	—	0·775	—	3·63	(22·2°)	—	—	—

by the later stereochemical developments of Baeyer's Strain Theory. Beyond this region normal conditions are found up to the sixteenth carbon atom.

Influence of Branching. In the case of the aliphatic hydrocarbons, single branching tends to diminish the viscosity, the *iso*paraffins (Thorpe

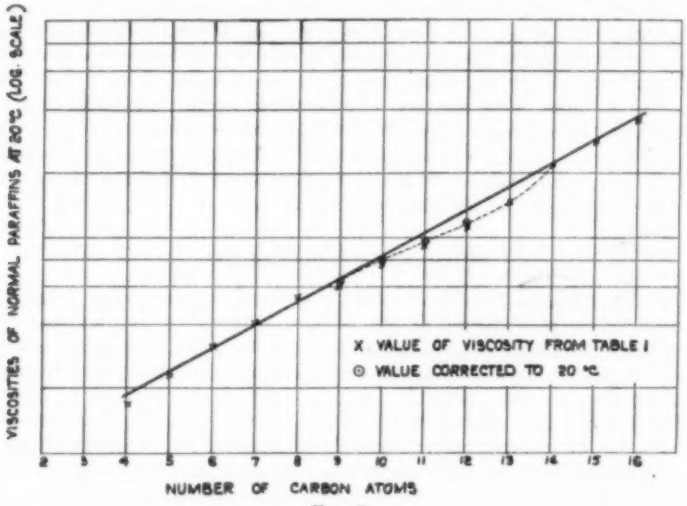
VISCOSITIES OF NORMAL PARAFFINS AT 20°C (LOG. SCALE)
X VALUE OF VISCOSITY FROM TABLE I
⊙ VALUE CORRECTED TO 20 °C.
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
NUMBER OF CARBON ATOMS

FIG. 1.

and Rodger) having slightly lower viscosities than the normal paraffins. This is in accordance with the general rule that the *iso*paraffins have lower boiling points, and melting points than the straight-chain isomers.

Table II gives the viscosities at different temperatures of normal and *iso*paraffins.

The viscosity–temperature curve for 3-methylpentane is practically

identical with that of the normal paraffin, and higher than that of 2-methylpentane. It seems probable, therefore, that the symmetry of the molecule has an important effect on the viscosity.

TABLE II.

Paraffin.	Viscosity in centipoises at				
	0° C.	20° C.	40° C.	60° C.	80° C.
Pentane	0·283	0·232	—	—	—
*iso*Pentane	0·280	0·228	—	—	—
Hexane	0·396	0·320	0·264	0·221	—
2-Methylpentane	0·371	0·300	0·247	0·208	—
3-Methylpentane	0·394	0·318	—	—	—
Heptane	0·519	0·410	0·334	0·276	0·232
*iso*Heptane	0·477	0·379	0·309	0·257	0·216

Introduction of two branch chains into the molecule has a striking effect. At low temperatures (0–20° C.) the viscosities of di*iso*propyl, $(CH_3)_2CH{\cdot}CH(CH_3)_2$, and 2 : 2-dimethylbutane, $CH_3{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CH_3$, are greater than that of the normal paraffin, and, in fact, the viscosity values approximate to that of the next higher *iso*paraffin, *iso*heptane. Similarly 2 : 7-dimethyloctane has a higher viscosity than *n*-decane. Three branch chains in the molecule, as in 2 : 2 : 3-trimethylbutane, result in an even greater increase in the viscosity.

Table III gives the viscosities of some normal paraffins, double-branched isomers and a three-branched heptane isomer.

TABLE III.

Paraffin.	Viscosity in centipoises at		
	0° C.	20° C.	30° C.
n-Hexane	0·396	0·320	0·290
2 : 2-Dimethylbutane	0·477	0·375	0·330
Di*iso*propyl	0·495	0·385	0·342
n-Decane	—	0·78 (22·3°)	—
2 : 7-Dimethyloctane	—	0·828 (25°)	—
n-Heptane	0·519	0·410	0·369
2 : 2 : 3-Trimethylbutane	0·802	0·599	0·506

The viscosity of a paraffin hydrocarbon with two-branch chains is greater than that of the normal parent hydrocarbon. Further, the viscosity of the symmetrically branched paraffin is greater than that of the unsymmetrical isomer, and this is in agreement with the relationship between the viscosity of the normal and the unsymmetrical *iso*paraffins.

Fig. 2, which is self-explanatory, indicates the relationships of the normal and branched-chain paraffins.

The Influence of Unsaturation. In comparison with the saturated aliphatic hydrocarbons, unsaturation by a single or by two double bonds diminishes the viscosity in the few cases for which data are available.

Table IV gives the viscosities of certain saturated and unsaturated aliphatic hydrocarbons.

TABLE IV.

Hydrocarbon.	Viscosity in centipoises at			
	0° C.	10° C.	20° C.	30° C.
*iso*Pentane	0·280	0·252	0·228	0·204
2-Methyl-Δ^2-butene	0·254	0·231	0·211	0·194
Isoprene	0·260	0·236	0·215	0·198
Hexane	0·396	0·355	0·320	0·290
Diallyl	0·339	0·303	0·274	0·249
2 : 2 : 3-Trimethyl butane	0·802	—	0·599	0·506
2 : 2 : 3-Trimethyl-Δ^3-butene	0·627	—	0·480	0·421

The influence of one double bond, so far as is known, is only slight, the introduction of a double bond into the *iso*pentane molecule reducing

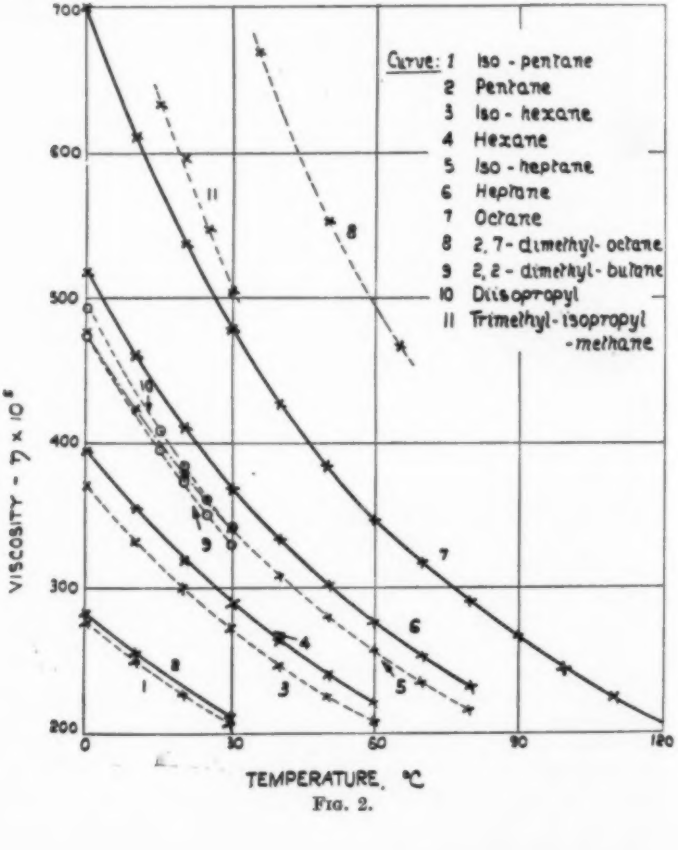

FIG. 2.

the viscosity approximately 8 per cent. at 0° C. Two double bonds cause a further reduction in viscosity, the diolefinic derivative of hexane, diallyl $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, having a viscosity at 0° C. 15 per cent. less than that of the saturated parent hydrocarbon. The conjugation of double bonds affects the viscosity in the opposite direction, tending to increase the viscosity. Thus isoprene, $CH_2{:}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{:}CH_2$, has a viscosity slightly higher than 2-methyl-Δ^2-butene, $CH_3{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH{\cdot}CH_3$, and its viscosity at 0° C. is only 7 per cent. less than that of the saturated parent hydrocarbon *iso*pentane.

Acetylenic unsaturation increases the viscosity of the aliphatic hydrocarbons to a considerable extent. Table V gives the viscosities of two acetylene hydrocarbons and their parent paraffins.

TABLE V.

Hydrocarbon.	Temperature. ° C.	Viscosity centipoises.
n-Octane	25	0·507
n-Hexylacetylene, C_8H_{14}	25	0·657
n-Undecane	22·7	0·94
n-Nonylacetylene, $C_{11}H_{20}$	25	2·0

Saturation of the nuclear double bonds of cyclic hydrocarbons raises the viscosity. In Table VI the viscosities of aromatic and naphthenic hydrocarbons are compared.

TABLE VI.

Hydrocarbon.	Viscosity in centipoises at			
	0° C.	10° C.	20° C.	30° C.
Benzene	0·902	0·759	0·649	0·562
*cyclo*Hexane	—	—	0·960	0·797
Toluene	0·768	0·667	0·586	0·520
Methyl*cyclo*hexane	0·976	0·836	0·722	0·627

This increase of viscosity with saturation is less pronounced with polycyclic hydrocarbons, as shown in Table VII.

TABLE VII.

Hydrocarbon.	Temperature. ° C.	Viscosity centipoises.
Naphthalene	80	0·886
Tetrahydronaphthalene	75	0·906
Decahydronaphthalene	75	1·08

In general it may be stated that, for both aliphatic and cyclic hydrocarbons, saturation of olefinic and aromatic hydrocarbons causes an increase in viscosity.

The influence of a double bond situated outside the ring of an aromatic hydrocarbon is, however, entirely different. In this case the viscosity is decreased by saturation of the double bond. This effect may be compared with that of conjugated double bonds in the aliphatic series.

Table VIII compares the viscosity of ethyl benzene with two unsaturated analogues.

TABLE VIII.

Hydrocarbon.	Temperature. ° C.	Viscosity centipoises.
Ethylbenzene	25	0·627
Styrene	25	1·11
Phenylacetylene	25	0·886

Although both the olefinic and acetylenic bonds in an alkyl chain attached to the benzene nucleus affect the viscosity in the same direction, an apparent anomaly is shown in that the acetylenic linkage does not increase the viscosity to the same extent as the olefinic. It is necessary here to consider the possibility of polymerization affecting the viscosity data. The effect of saturation may be to increase viscosity in all cases, but with relatively unstable compounds such as styrene and phenylacetylene *polymerization* may entirely mask the decrease due to unsaturation. Alternatively, unsaturation may cause *association* of the hydrocarbon, with consequent increase in viscosity. It may be considered, therefore, that the primary effect of unsaturation is to decrease viscosity, but that the factors of association or polymerization, characteristic of unsaturation, may have a greater effect resulting in an actual increase in viscosity.

Influence of Cyclic Structure. Cyclic structure in the molecule increases both viscosity and density considerably, and this statement holds when considering both naphthenic and aromatic hydrocarbons as shown by Tables IX and X.

TABLE IX.

Naphthenic Structure.

Hydrocarbon.	Density at 20° C.	Viscosity in centipoises at				
		0° C.	15° C.	20° C.	25° C.	30° C.
Pentane	0·631	0·283	0·242	0·232	0·220	0·212
*cyclo*Pentane	0·754	0·572	0·477	0·456	0·427	0·406
Hexane	0·660	0·396	0·337	0·320	0·305	0·290
*cyclo*Hexane	0·779	—	1·043	0·960	0·884	0·797
Heptane	0·684	0·519	0·434	—	—	0·369
Methyl*cyclo*hexane	0·764	0·976	0·780	—	—	0·627

The condensation of benzene nuclei and of *cyclo*hexane nuclei still further increases the viscosity. In Table XI the viscosities of naphthalene and its hydrogenated derivative are considerably higher than would be accounted for by their increased molecular weight in comparison with their monocyclic analogues.

TABLE X.

Aromatic Structure.

Hydrocarbon.	Density at 20° C.	Viscosity in centipoises at				
		0° C.	20° C.	40° C.	60° C.	80° C.
n-Hexane	0·660	0·396	0·320	0·264	0·221	—
Benzene	0·879	0·902	0·649	0·492	0·390	—
n-Heptane	0·684	0·519	0·410	0·334	0·276	0·232
Toluene	0·866	0·768	0·586	0·466	0·381	0·318
n-Octane	0·701	0·703	0·538	0·428	0·350	0·290
Ethylbenzene	0·868	0·874	0·666	0·529	0·432	0·360

TABLE XI.

Hydrocarbon.	Temperature. ° C.	Viscosity centipoises.
Benzene	80	0·327
Naphthalene	80	0·886
*cyclo*Hexane	25	0·884
Tetrahydronaphthalene	25	2·41

The increase in viscosity due to accumulation of aromatic rings in the molecule is well shown by the phenylmethanes, a viscosity of 3·22 centipoises at 100° C. being exhibited by triphenyl methane (Table XII).

TABLE XII.

Hydrocarbon.	Temperature. ° C.	Viscosity centipoises.
Phenylmethane, C_7H_8	100	0·269
Diphenylmethane, $C_{13}H_{12}$	100	0·83
Triphenylmethane, $C_{19}H_{16}$	100	3·22

The compound $(CH_3)_3C_6H_2—\overset{CH_3}{\underset{CH_3}{C}}—C_6H_2(CH_3)_2$, synthesized by Kramer and Spilker,[16] is a viscous oil, approximately 775 centipoises at 15° C. These investigators attributed the high viscosity to the accumulation of methyl groups in the molecule, but the above data indicate that the aromatic structure is more probably the predominant cause of this increase in viscosity.

The effect of condensed cyclic structure in increasing the viscosity is substantiated by consideration of benzenoid and condensed benzenoid hydrocarbons with long aliphatic side-chains. Oils have been synthesized by the Friedel–Crafts reaction from the condensation of aromatic hydrocarbons with chlorinated paraffin wax, and using the same chlorinated paraffin wax with benzene and naphthalene as cyclic components the hydrocarbon lubricating oils obtained had the viscosities shown in Table XIII.

TABLE XIII.

Aromatic component.	Viscosity at 100° F.
Benzene	298 centistokes.
Toluene	440 "
Naphthalene	815 "

AROMATIC AND *cyclo*PARAFFINIC HYDROCARBONS.

The first members of the aromatic and *cyclo*hexane series (6-ring) show anomalous behaviour, benzene and *cyclo*hexane having higher viscosities than the succeeding homologues, toluene and methyl*cyclo*hexane. As a general rule, the addition of methyl groups increases the viscosity. In the *cyclo*pentane series the viscosities are in the order of their molecular weights, and these points are illustrated by Table XIV.

TABLE XIV.

Hydrocarbon.	Viscosity in centipoises at						
	0° C.	15° C.	20° C.	30° C.	40° C.	60° C.	80° C.
Benzene	0·902	—	0·649	—	0·492	0·390	0·327
Toluene	0·768	—	0·586	—	0·466	0·381	0·318
*cyclo*Hexane	—	1·043	0·960	0·797	—	—	—
Methyl*cyclo*hexane	—	0·78	—	—	—	—	—
*cyclo*Pentane	0·572	0·477	0·456	0·406	—	—	—
Methyl*cyclo*pentane	0·665	0·545	0·521	0·456	—	—	—

The influence of the orientation of the methyl groups in the nucleus on the viscosity is analogous to its effect upon the chemical properties of the *ortho*-, *meta*-, and *para*-substituted compounds, as the *meta*-substituted derivatives frequently exhibit exceptional behaviour. The viscosity-temperature curve for *meta*-xylene is not intermediate between the curves for the *ortho*- and *para*-xylenes, but lies below them, as may be seen from Table XV.

TABLE XV.

Hydrocarbon.	Viscosity in centipoises at						
	0° C.	20° C.	40° C.	60° C.	80° C.	100° C.	120° C.
o-Xylene	1·102	0·807	0·623	0·500	0·411	0·345	0·294
p-Xylene	—	0·843	0·508	0·412	0·345	0·292	0·251
m-Xylene	0·802	0·615	0·491	0·404	0·339	0·289	0·250

The dimethyl*cyclo*hexanes, prepared by the hydrogenation of the corresponding xylenes, also show the anomalous behaviour of the *meta*-derivative. The physical properties of the dimethyl*cyclo*hexanes are dependent on the nature of the catalyst—nickel or platinum—used in their preparation (Table XVI). According to Chavanne,[12] this is due to the formation of

mixtures of stereoisomers, the catalyst influencing the relative proportion of *cis* and *trans* forms present.

TABLE XVI.

Dimethylcyclohexane.	Catalyst.	Density.	Viscosities in centipoises at		
			0° C.	15° C.	30° C.
Ortho-	Pt	0·814	1·604	1·195	0·916
Para-	Pt	0·8075	1·307	0·994	0·776
Meta-	Pt	0·7852	0·874	0·702	0·578
Ortho-	Ni	0·7975	1·170	0·905	0·722
Para-	Ni	0·787	1·05	0·813	0·655
Meta-	Ni	0·789	0·932	0·750	0·607

Addition of an aliphatic chain to the benzene nucleus increases the viscosity in proportion to the number of carbon atoms in the chain (Table XVII), benzene itself, as noted previously, being anomalous.

TABLE XVII.

Hydrocarbon.	Viscosity in centipoises at				
	0° C.	20° C.	25° C.	40° C.	60° C.
Toluene	0·768	0·586	—	0·466	0·381
Ethylbenzene	0·874	0·666	0·627	0·529	0·432
n-Propylbenzene	—	—	0·793	—	—
n-Butylbenzene	—	—	1·05	—	—

Again, introduction of methyl groups into a polycyclic nucleus increases the viscosity (Table XVIII).

TABLE XVIII.

Hydrocarbon.	Temperature ° C.	Viscosity centipoises.
1-Methylnaphthalene	20	3·38
1 : 6-Dimethylnaphthalene	20	3·63
Decahydronaphthalene	20	2·84

The viscosities of the methylnaphthalene derivatives cannot be compared with that of naphthalene at this temperature, but for comparison purposes the viscosity of decahydronaphthalene is given. This saturated derivative has a greater viscosity than naphthalene at temperatures above the melting point of naphthalene.

INFLUENCE OF MOLECULAR WEIGHT AND VOLUME.

The molecular volume (Mv) and molecular surface ($Mv)^{\frac{2}{3}}$ of hydrocarbons and hydrocarbon derivatives were considered by Thorpe and Rodger,[3] who found that when the viscosities (multiplied by either of these factors) are compared at temperatures of equal change of viscosity with temperature,

the increment for each CH_2 becomes fairly regular. In an homologous series this increment for the molecular surface factor $(\eta \times (Mv)^{\frac{2}{3}} \times 10^4)$ is approximately 120 for temperatures corresponding to a slope of 0·0000323, of the viscosity–temperature curve.

Dunstan [1] submitted that the ratio $\frac{\text{Viscosity}}{\text{Molecular volume}}$ has low values, not differing greatly for non-associated liquids, whilst the ratio is much higher for associated liquids, particularly those containing hydroxyl groups.

Attempts to represent the mechanism of viscosity as friction between molecular surfaces are considered by McLeod [5] to be false analogies, and he states that the viscosity of a liquid is a linear function of the molecular weight, and varies inversely as the "free space" within the liquid. The "free space," or space not occupied by the molecules, is a constitutive property, for isomers having different viscosities have also different "free spaces," the differences being in the right direction as shown by the data for normal and *iso*hexane in Table XIX.

TABLE XIX.

	Temperature. ° C.	Free space per unit volume. (McLeod.)	Viscosity centipoises.
n-Hexane . . .	0	0·1240	0·396
*iso*Hexane . . .	0	0·1260	0·371

THE VISCOSITY–TEMPERATURE RELATIONSHIP OF HYDROCARBONS.

In addition to the factor of viscosity, consideration must be given to the viscosity–temperature curves of the various classes of hydrocarbons and their relationship to constitution.

Hugel [4] observed that with oils having the same viscosity at a low temperature, the oil that showed the best viscosity–temperature stability (*i.e.* the oil with the highest viscosity at a higher temperature) was that having the greatest molecular weight, and he states that molecular volume is of greater importance than molecular weight. It seems probable, however, that molecular surface, free space, stereochemical structure and molecular association are essential factors in determining the viscosity–temperature stability.

Paraffin Hydrocarbons. The viscosity–temperature curves for the normal paraffins are approximately parallel (Fig. 2), the gradient, however, at any single temperature depending upon the molecular weight. Single branching, which lowers the viscosity slightly, does not affect noticeably the gradient of the viscosity–temperature curve, as shown by the curves for the *iso*paraffins which are closely parallel to those of the normal paraffins. The presence of two-branch chains in the molecule raises the viscosity, and at the same time causes an appreciable increase in the gradient of the curve (Fig. 2). Di*iso*propyl and 2 : 2-dimethylbutane show greater changes of viscosity for a given temperature change than *n*-hexane.

Three-branch chains in the molecule, as in 2 : 2 : 3-trimethylbutane,

cause an even greater increase in viscosity and increase in the gradient of the viscosity–temperature curve.

When the logarithm of the viscosity is plotted against temperature (in ordinary units), the curves obtained approximate to a straight-line relationship, the linear deviation being greater with the higher molecular weights. On Figs. 2 and 3 are plotted the viscosity–temperature curves for various paraffins.

In general, it may be stated that viscosity–temperature stability increases with chain-length, and for isomers decreases with increased branching. This is supported by the investigations of Sullivan, Voorhees, Neeley and Shankland [6] on the polymerization of olefines, and by the

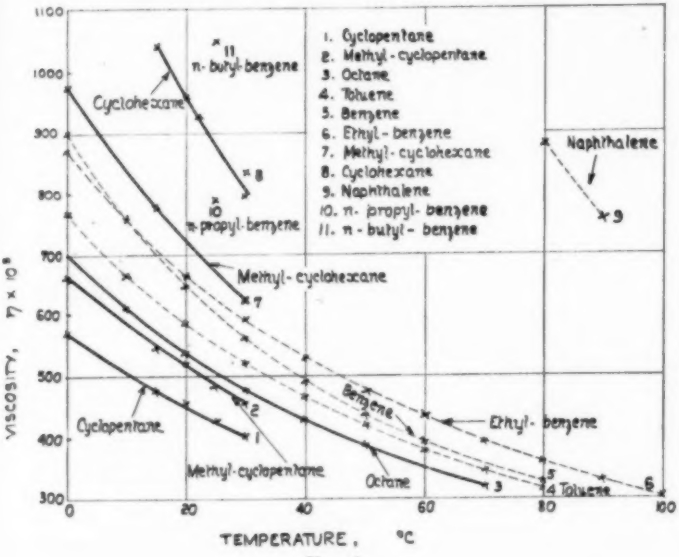

FIG. 3.

work of Yamaguchi [7] on the temperature coefficient of viscosity and the association of high-molecular-weight liquids.

Cyclic Hydrocarbons. The curve for benzene is steeper than the curves for the paraffin hydrocarbons. Higher homologues of the aromatic series show less steep viscosity gradients, those for toluene and ethylbenzene being approximately parallel to the curves for the normal paraffins.

*cyclo*Hexane also has a steep curve similar to that for benzene, and it will be seen from Fig. 3 that the curve for methyl*cyclo*hexane is approximately parallel to that for toluene. *cyclo*Pentane and methyl*cyclo*pentane have viscosity–temperature curves which are parallel to those of the normal paraffins. Naphthalene and its hydrogenated derivatives, tetrahydronaphthalene and decahydronaphthalene, exhibit a high rate of change of viscosity with temperature, much more so than benzene. This is illustrated by Fig. 4.

Influence of Unsaturation on Viscosity–Temperature Relationships.

In the case of aliphatic hydrocarbons, unsaturation does not affect the viscosity–temperature stability so far as is known. The unsaturated hydrocarbons 2-methyl-Δ^2-butene, isoprene and diallyl have viscosity-

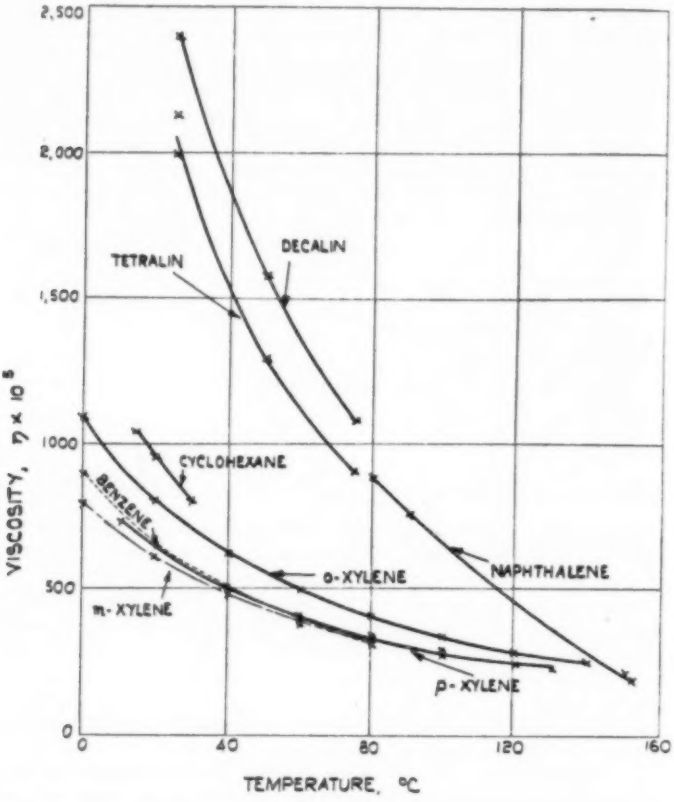

Fig. 4.

temperature curves similar to the corresponding paraffins, *iso*pentane and hexane.

Again with the cyclic hydrocarbons, unsaturation has little effect on the rate of change of viscosity with temperature, the curves for the aromatics resembling those of the naphthenes. With the polycyclic hydrocarbons, unsaturation modifies to a slight extent the viscosity–temperature stability. Tetrahydronaphthalene and decahydronaphthalene have slightly lower viscosity–temperature gradients than naphthalene, as shown by Fig. 5.

Association and Viscosity–Temperature Stability.

The rate of change of viscosity with change of temperature is influenced greatly by association of the hydrocarbon. The degree of association in liquids decreases with increase of temperature, and therefore temperature change will be accompanied by a change in viscosity due to alteration of the association factor, as well as the normal viscosity change of the unassociated liquid.

The lower hydrocarbons as a class have little tendency to association, but small differences in the degree of association have an important effect on the temperature coefficient of viscosity. Values of the association

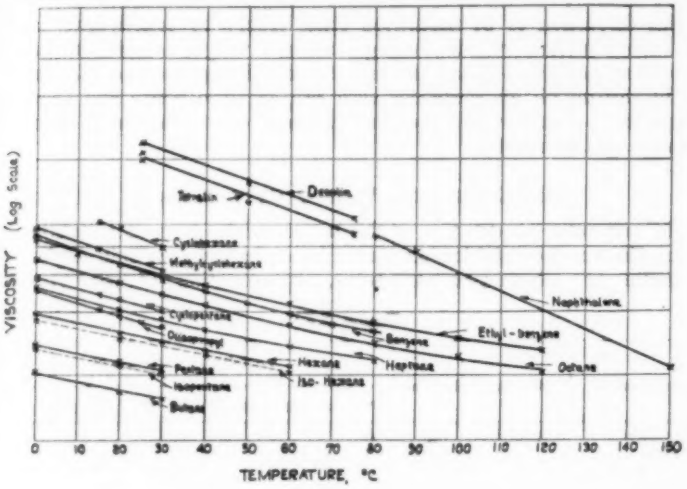

Fig. 5.

factor calculated by McLeod,[5] Ramsay and Shields,[8] Bingham[9] and Traube[10] are given in Table XX.

Table XX.

Hydrocarbon.	Association factor.			
	McLeod.	Ramsay and Shields.	Bingham.	Traube.
Octane . . .	0·93	0·93	—	—
Benzene . . .	1·37	1·01	1·14	1·05
Toluene . . .	1·08	—	1·06	—
Ethylbenzene . .	0·91	—	1·02	—
o-Xylene . . .	1·02	—	1·06	—
m-Xylene . . .	0·92	—	1·00	—

The difference in the slopes of the viscosity–temperature curves for benzene and toluene can be accounted for in part by the difference in the

degree of association, benzene, being more highly associated than toluene, has an abnormally high viscosity and viscosity–temperature gradient. The above association data should be taken into account when studying the viscosity values mentioned in this paper.

Although the simpler hydrocarbons as a rule undergo association to a small extent, those of higher molecular weight may be highly associated (Staudinger,[11] Yamaguchi [7]). The hydrocarbons present in lubricating-oil fractions form molecular aggregates approaching colloidal dimensions, so that a lubricating oil may be considered as a polyphase system in which hydrocarbon molecular aggregates are dispersed in a hydrocarbon medium of simpler molecular structure.

The viscosity characteristics of the lower hydrocarbons have been shown in this discussion to be influenced considerably by constitution, and it has been seen that with increasing molecular weight association tends to become an important factor affecting the physical properties. A study of the lubricating-oil hydrocarbons with respect to viscosity and viscosity-temperature stability will therefore demand consideration of both constitution and association.

High-Molecular-Weight Hydrocarbons.

The molecular constitution of the hydrocarbons present in lubricating-oil fractions may consist to a greater or less extent of paraffinic, naphthenic, aromatic or polynuclear structures. Examination of the viscosity-

Table XXI.

Hydrocarbon.	Structure.	Formula.	Viscosity in centipoises at								
			20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Tricaprylene.	Aliphatic.	$C_{24}H_{48}$	29·5	17·4	11·5	9·0	6·4	—	—	—	—
Squalene.	,,	$C_{30}H_{50}$	—	12·4	9·1	6·8	5·2	4·2	3·7	—	—
7 : 12-Dimethyl-9 : 10-*n*-dihexyl-octodecane.	,,	$C_{32}H_{66}$	—	23·3	16·0	11·4	8·1	5·8	4·1	—	—
Methyloctyltetracosylene.	,,	$C_{33}H_{64}$	—	13·8	9·7	7·0	5·1	3·8	3·0	—	—
16-*n*-Butylhentriacontane.	,,	$C_{35}H_{72}$	42·0	27·5	19·0	13·5	10·0	7·7	6·1	4·9	4·1
Dimethyltetrahexyldocosane.	,,	$C_{40}H_{82}$	—	123	66·0	40·0	26·0	18·0	13·0	—	—
1 : 1-Diphenylhexadecane.	Alkyl aromatic.	$C_{28}H_{42}$	47·1	28·9	18·9	13·0	9·4	7·0	5·5	4·5	3·7
1 : 1-Di*cyclo*hexylhexadecane.	Alkyl naphthenic.	$C_{28}H_{54}$	70·7	41·4	25·8	17·4	12·3	8·9	6·9	5·5	4·4
1-*cyclo*Hexyl-2-hexahydrobenzylheptadecane.	,,	$C_{30}H_{58}$	62·9	37·8	24·3	16·0	11·6	8·4	6·5	5·0	4·3
1-Phenyl-2-benzylheptadecane.	Alkyl aromatic.	$C_{30}H_{46}$	81·5	48·4	28·1	18·4	12·7	9·0	7·0	5·0	4·4
Dimethyl*iso*butyldihydronaphthalene.	Alkylated polynuclear aromatic.	$C_{16}H_{24}$	59·9	31·2	20·1	12·8	8·0	5·5	—	—	—
Tetrahydrodi*iso*butylnaphthalene.	,,	$C_{18}H_{32}$	40·3	22·0	14·0	9·0	6·0	4·4	—	—	—
Di*iso*butylnaphthalene.	,,	$C_{18}H_{24}$	47·6	24·0	14·0	9·0	6·0	4·4	—	—	—
Dihydrodiethylanthracene.	Alkylated polynuclear aromatic.	$C_{18}H_{20}$	157	70	28	17	11	7·3	—	—	—
Dihydrodi*iso*amylanthracene.	,,	$C_{24}H_{32}$	5,086	—	420	184	80·0	40	25·0	—	—
Dihydrodioctylanthracene.	,,	$C_{30}H_{44}$	—	520	232	112	57·0	—	—	—	—

temperature curves of high molecular weight hydrocarbons of known structure will show to what extent the general rules relating viscosity and constitution of the simpler low molecular weight hydrocarbons are followed by the more complex compounds, and such comparison may throw light upon the constitution of the various classes of petroleum lubricating-oil hydrocarbons. Hydrocarbons of high molecular weight have been synthesized by several investigators [13, 14, 15] and the physical properties

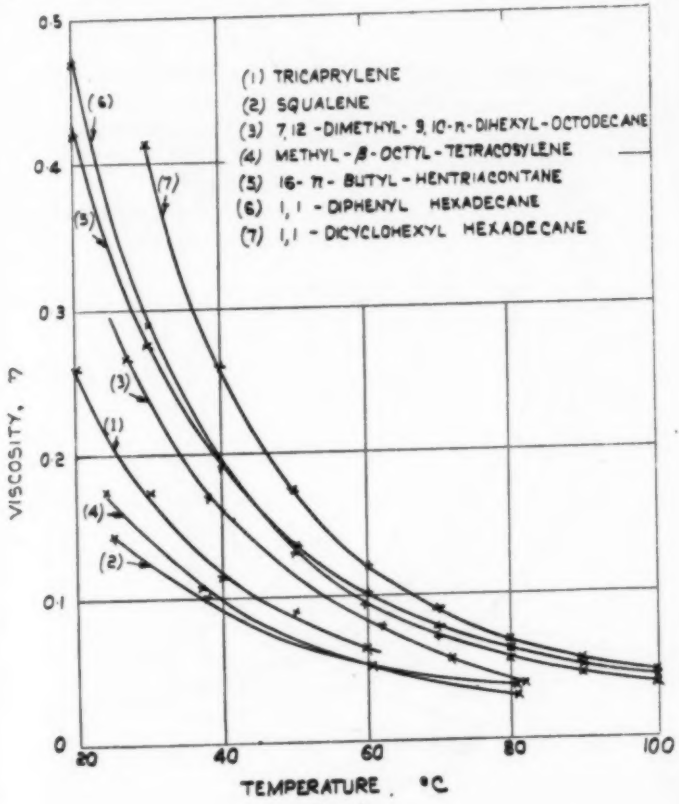

FIG. 6.

determined. The viscosity–temperature data for these hydrocarbons are given in Table XXI, the corresponding curves being shown in Figs. 6, 7 and 8. From these it is seen that the aliphatic hydrocarbons have lower viscosities than corresponding hydrocarbons with cyclic structure.

No conclusions can be reached as to the effect of unsaturation and branching, because these synthetic aliphatic hydrocarbons have widely dissimilar structures and, with the examples given in the table, it is impossible to isolate the effects due to number, position and length of

branch chains and position of the olefinic bond. The long-chain structure of 16-*n*-butylhentriacontane is accompanied by a viscosity–temperature curve which is less steep than the curves for the comparable hydrocarbons dimethyldihexyloctadecane and tricaprylene which have more highly branched structures.

The introduction of simple benzene and naphthene rings into the molecule raises the viscosity to a moderate extent, but is accompanied by

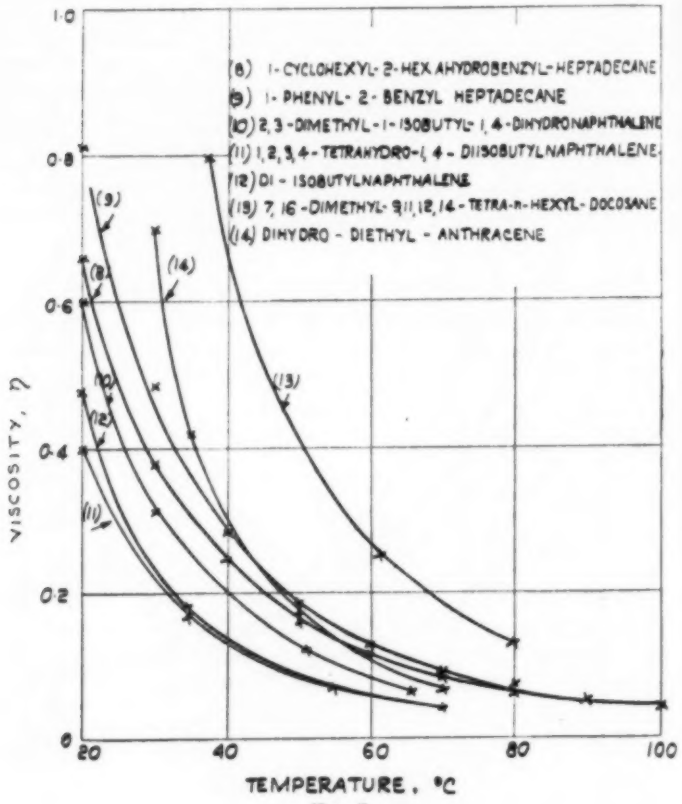

FIG. 7.

only a very slight increase in the gradient of the viscosity–temperature curve. This is illustrated by the curves for 1 : 1-diphenylhexadecane, 1 : 1-di*cyclo*hexylhexadecane, 1-phenyl-2-benzylheptadecane and 1-*cyclo*hexyl-2-hexahydrobenzylheptadecane. These four hydrocarbons may be considered as *n*-hexadecane structures to which have been attached in the 1 : 1-position phenyl, *cyclo*hexyl, benzyl and hexahydrobenzyl groupings respectively. The curve for the phenyl-substituted compound is closely parallel to that of the *cyclo*hexyl derivative, and the benzyl and hexahydro-

benzyl derivatives also have similar viscosity–temperature curves. Hydrogenation of the cyclic component does not alter the viscosity in the same direction for the phenyl and benzyl derivatives. The aromatic and naphthenic derivatives have similar viscosities and viscosity–temperature stabilities.

The introduction of polycyclic structure into the hydrocarbon molecule results in a marked decrease of the viscosity–temperature stability.

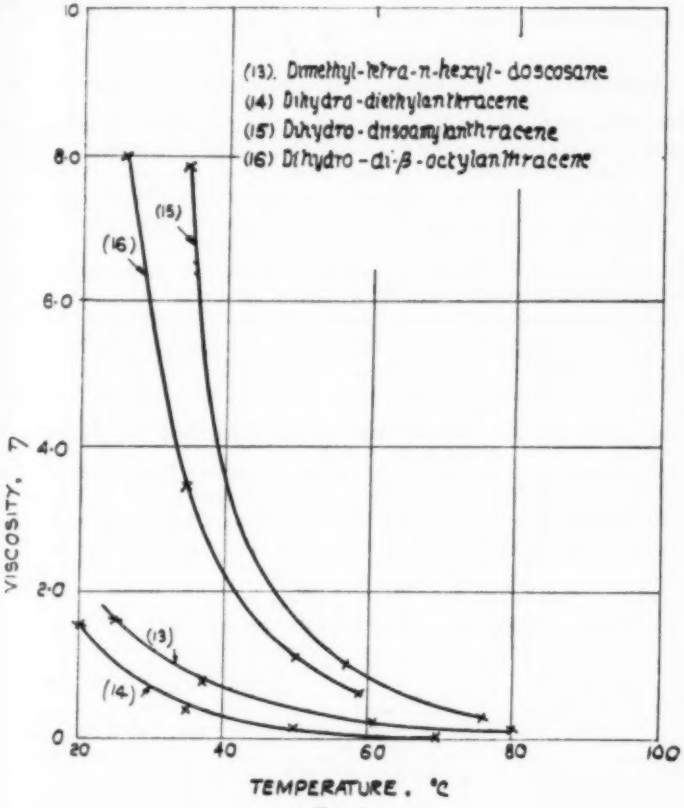

FIG. 8.

Naphthalene derivatives have moderate viscosities at normal temperature and steep viscosity–temperature curves. Alkylated anthracenes have much higher viscosities at ordinary temperature and still lower viscosity–temperature stabilities. In Fig. 8 the steep gradients of the curves for the anthracene derivatives (Curves 15 and 16) are in contrast to the flat curve of the aliphatic hydrocarbon, dimethyltetrahexyldocosane (Curve 13). Dihydrodiethylanthracene has a flat curve in Fig. 8; this, however, is due to its low viscosity, and when compared in Fig. 7 with hydro-

carbons of similar viscosity the anthracene derivative is seen to have a relatively poor viscosity–temperature stability.

In summarising, it may be stated that the aliphatic hydrocarbons have low viscosities in relation to the number of carbon atoms in the molecule, and very good viscosity–temperature stabilities. Hydrocarbons containing simple cyclic groups have higher viscosities and good viscosity temperature stabilities, but the introduction of polycyclic structure into the molecule increases the viscosity to a marked extent and depresses the viscosity–temperature stability.

Evaluation of the Viscosity–Temperature Relationship.

The relationship between viscosity and temperature is most simply illustrated by graphical means through the viscosity–temperature curve on appropriate co-ordinates. It has already been pointed out that this method does not afford a satisfactory comparison for hydrocarbons of widely differing viscosity, and, in addition, it does not give any numerical evaluation of the change in viscosity with temperature.

The change in viscosity for any given increment of temperature, in the case of any hydrocarbon, is primarily dependent on the viscosity. As the temperature increases, with corresponding decrease in viscosity, the same increments of temperature are accompanied by progressively smaller changes of viscosity. Viscous hydrocarbons, as a consequence, show relatively large viscosity changes when compared with less viscous hydrocarbons over the same temperature range. Therefore the function $\frac{d\eta}{dt}$, denoting change in viscosity with temperature, for any hydrocarbon, varies continuously according to the viscosity and temperature, and it is not possible satisfactorily to compare viscosity–temperature coefficients unless the viscosity and temperature also are taken into consideration.

Table XXII.

Fractional Viscosity–Temperature Coefficient.

Hydrocarbon.	Formula.	$\frac{\Delta\eta}{\Delta t}\cdot\frac{1}{\eta}$ or $\frac{\eta_{(t-10)}-\eta_{(t+10)}}{20\eta_t}$ at						
		30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
Tricaprylene	$C_{24}H_{48}$	0·0414	0·0365	0·0284	—	—	—	—
Squalene	$C_{30}H_{50}$	—	0·0308	0·0287	0·0250	0·0179	—	—
Dimethyl-*n*-dihexyloctadecane	$C_{32}H_{66}$	—	0·0372	0·0347	0·0346	0·0345	—	—
Methyloctyltetracosylene	$C_{33}H_{66}$	—	0·0351	0·0329	0·0314	0·0277	—	—
16-*n*-Butylhentriacontane	$C_{35}H_{72}$	0·0418	0·0369	0·0334	0·0290	0·0254	0·0230	0·0204
Dimethyltetrahexyldocosane	$C_{36}H_{74}$	—	0·0630	0·0500	0·0424	0·0362	—	—
1 : 1-Diphenylhexadecane	$C_{28}H_{42}$	0·0488	0·0421	0·0365	0·0319	0·0279	0·0227	0·0209
1 : 1-Di*cyclo*hexylhexadecane	$C_{28}H_{54}$	0·0540	0·0465	0·0388	0·0346	0·0304	0·0247	0·0227
1-*cyclo*Hexyl-2-hexahydrobenzylheptadecane	$C_{29}H_{56}$	0·0510	0·0449	0·0397	0·0328	0·0304	0·0262	0·0220
1-Phenyl-2-benzylheptadecane	$C_{30}H_{48}$	0·0550	0·0535	0·0419	0·0370	0·0317	0·0286	0·0260
Dimethyl*iso*butyldihydronaphthalene	$C_{18}H_{24}$	0·0640	0·0458	0·0473	0·0456	—	—	—
Tetrahydrodi*iso*butylnaphthalene	$C_{18}H_{28}$	0·0600	0·0465	0·0445	0·0384	—	—	—
Di*iso*butylnaphthalene	$C_{18}H_{24}$	0·0700	0·0535	0·0445	0·0384	—	—	—
Dihydrodiethylanthracene	$C_{18}H_{20}$	0·0920	0·0945	0·0500	0·0441	—	—	—
Dihydrodi*iso*amylanthracene	$C_{26}H_{36}$	—	—	0·0925	0·0900	0·0690	—	—
Dihydrodi-β-octylanthracene	$C_{38}H_{44}$	—	0·0880	0·0780	—	—	—	—

The fractional viscosity–temperature coefficient, $\frac{1}{\eta} \cdot \frac{\Delta\eta}{\Delta t}$ has been calculated for a number of high-molecular-weight hydrocarbons, the results being given in Table XXII. The value of this fractional viscosity–temperature coefficient was obtained by taking the change in absolute viscosity over a 20° C. interval and dividing the average change per degree by the viscosity

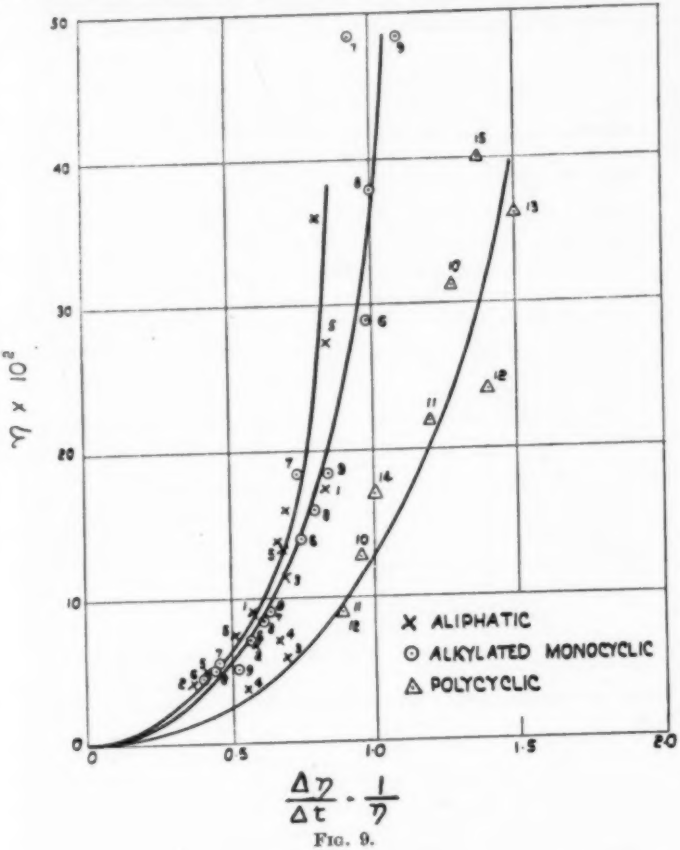

FIG. 9.

at the mean temperature. Thus $\frac{\eta_{20} - \eta_{40}}{20 \times \eta_{30}}$ was taken as the fractional temperature coefficient at 30° C.

Comparison of these fractional viscosity–temperature coefficients for high- and low-molecular-weight hydrocarbons indicates that this function is still dependent on viscosity, the values for the high-molecular-weight hydrocarbons being much larger than those of the simpler low-molecular-weight homologues at corresponding temperatures. The values obtained

for the sixteen high-molecular-weight hydrocarbons show that this function is constitutive, being relatively low for aliphatic hydrocarbons, moderate for compounds containing simple cyclic structures, and high for polycyclic hydrocarbons. As the temperature is increased, the fractional temperature coefficient decreases, and Figs. 9 and 10, in which $\frac{1}{\eta} \cdot \frac{\Delta\eta}{\Delta t}$ is plotted against η and log η, respectively, illustrate the differences between the three classes of hydrocarbons. In Fig. 10 the fractional temperature

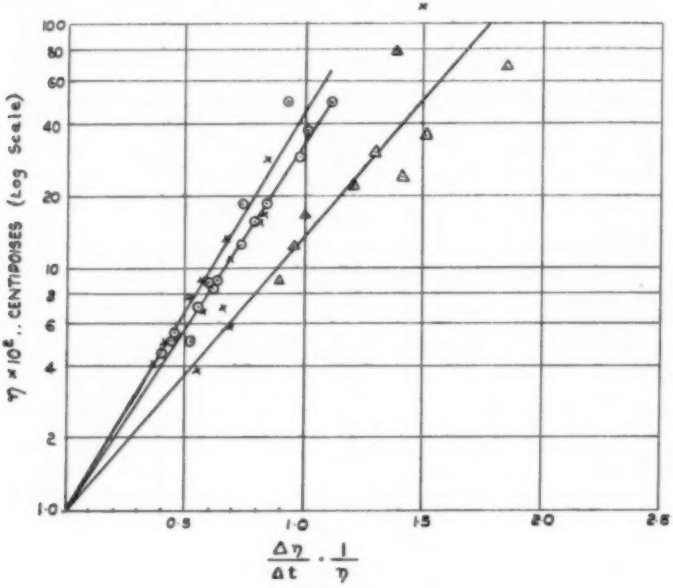

FIG. 10.

coefficient is seen to have a linear relationship with the logarithm of the viscosity; *i.e.*

$$\frac{1}{\eta} \cdot \frac{\Delta\eta}{\Delta t} \propto \log \eta$$

or

$$\frac{\Delta\eta}{\Delta t} \cdot \frac{1}{\eta \log \eta} = a \text{ constant.}$$

This latter function, calculated for various high-molecular-weight hydrocarbons at different temperatures, is given in Table XXIII, and is approximately constant for the same hydrocarbon. The aliphatic hydrocarbons, together with those containing simple cyclic structure, have a fairly uniform value ranging from 0·03 to 0·04 approximately, 16-*n*-butylhentriacontane, with predominant straight-chain structure, has the low value of 0·029, whilst the hydrocarbons with branched and simple cyclic components have

higher values. The polycyclic hydrocarbons have higher values ranging from 0·04 to 0·05; but it should be noted that dihydrodi-β-octyl-anthracene, with a high proportion of straight-chain alkyl components, has the moderate value of 0·038.

TABLE XXIII.

Modified Fractional Viscosity–Temperature Coefficient.

Hydrocarbon.	$\frac{1}{\eta \log \eta} \cdot \frac{\Delta\eta}{\Delta t}$ at							Average Value.	Deviation %.
	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.		
Tricaprylene	0·0334	0·0344	0·0298	—	—	—	—	0·0325	−8 to +6
Squalene	—	0·0323	0·0345	0·0349	0·0286	—	—	0·0326	−12 to +7
Dimethyl-*n*-dihexyloctadecane	—	0·0301	0·0328	0·0381	0·0452	—	—	0·0367	−15 to +23
Methyloctyltetracosylene	—	0·0355	0·0389	0·0443	0·0476	—	—	0·0416	±15
16-*n*-Butylhentriacontane	0·0290	0·0288	0·0295	0·0290	0·0286	0·0292	0·0296	0·0291	±1·7
Dimethyltetrahexyldocosane	—	0·0347	0·0312	0·0299	0·0288	—	—	0·0311	−7 to 11
1 : 1-Diphenylhexadecane	0·0334	0·0330	0·0327	0·0328	0·0330	0·0307	0·0307	0·0330	−7 to +1
1 : 1-Dicyclohexylhexadecane	0·0334	0·0329	0·0313	0·0317	0·0319	0·0294	0·0307	0·0316	−7 to 6
1-*cyclo*Hexyl-2-hexahydrobenzylheptadecane	0·0323	0·0324	0·0329	0·0307	0·0329	0·0322	0·0315	0·0321	−4 to +2·5
1-Phenyl-2-benzylheptadecane	0·0327	0·0369	0·0331	0·0335	0·0332	0·0338	0·0372	0·0343	−5 to +8
Dimethyl*iso*butyldihydronaphthalene	0·0355	0·0351	0·0427	0·0504	—	—	—	0·0409	−13 to +23
Tetrahydrodi*iso*butylnaphthalene	0·0447	0·0406	0·0466	0·0493	—	—	—	0·0453	−10 to +9
Di*iso*butylnaphthalene	0·0507	0·0467	0·0466	0·0493	—	—	—	0·0483	−3·5 to +5
Dihydrodiethylanthracene	0·0498	0·0652	0·0407	0·0423	—	—	—	0·0495	−17 to 31
Dihydrodi*iso*amylanthracene	—	—	0·0408	0·0473	0·0431	—	—	0·0437	−7 to +8
Dihydrodi-β-octylanthracene	—	0·0372	0·0380	—	—	—	—	0·0376	±1

The same coefficient has been calculated for five different oils at different temperatures, and the results, given in Table XXIV, show that the function is fairly constant for these oils as for pure hydrocarbons.

The expression $\frac{\Delta v}{\Delta t} \cdot \frac{1}{v \log v}$ may likewise be calculated for viscosities given in kinematic units, and in Table XXV this modified coefficient is given for three oils of Pennsylvanian type and for three of Gulf Coast origin. The fractional viscosity–temperature coefficients of the Gulf oils are higher than those for the Pennsylvanian oils of comparable viscosity. The function is, however, only very approximately constant, and decreases slightly with increase in temperature. At any given temperature there is a marked difference in the value for the two types of oil, the Pennsylvanian oils having the lower values.

The expression may be regarded as a simple form of index, derived from the coefficient of viscosity change with temperature, and affording a means for the classification of viscous hydrocarbons according to their chemical types. It is, in this respect, comparable with the well-known " Viscosity

TABLE XXIV.

Oil.	Viscosity in centipoises at									Modified fractional viscosity–temperature coefficient $\frac{\Delta\eta}{\Delta t}\cdot\frac{1}{\eta \log \eta}$ at							Average Value.
	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.*	80° C.	90° C.*	100° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	
Castor † .	1320	684	343	158·5	91·2	59·9	41·2	27·7	19·46	0·0252	0·0302	0·0361	0·0275	0·0235	0·0242	0·0272	0·0277
S † . .	1380	708	363	204	119	75·2	50	34·9	25·24	0·0249	0·0271	0·0261	0·0261	0·0245	0·0237	0·0230	0·0251
W † .	355	150	80	47·86	29·2	18·89	12·92	9·64	7·37	0·0421	0·0335	0·0316	0·0339	0·0341	0·0322	0·0293	0·0338
No. 3 † .	700	316	166	96·6	61·0	38·5	25·7	18·24	13·42	0·0310	0·0298	0·0274	0·0257	0·0289	0·0279	0·0266	0·0282
Penna H_1 ‡	470	240	133	79·7	50·6	33·8	23·6	17·0	12·6	0·0295	0·0283	0·0273	0·0266	0·0262	0·0259	0·0263	0·0271

* Interpolated values.
† Viscosities obtained by Rowell and Finlayson, *J.I.P.T.*, 1928, **14**, 402.
‡ Absolute viscosities calculated from kinematic using temperature coefficient of density 0·00065 per 1° C.

TABLE XXV.

Oil.	Viscosity in centistokes at									Fractional viscosity–temperature coefficient $\frac{\Delta v}{\Delta t}\cdot\frac{1}{v}$ at							Modified fractional viscosity–temperature coefficient $\frac{\Delta v}{\Delta t}\cdot\frac{1}{v \log v}$ at						
	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
Penna H_1 (V.I. = 100). 80 secs. Saybolt at 210° F. .	523	273	153	92·2	59·0	39·7	27·9	20·3	15·2	0·0694	0·0590	0·0510	0·0445	0·0392	0·0348	0·0313	0·0285	0·0270	0·0259	0·0251	0·0245	0·0241	0·0239
Penna H_2 (V.I. = 100). 120 Saybolt at 210° F.	1,240	610	311	178	109	70·0	47·7	33·5	24·5	0·0760	0·0695	0·0568	0·0496	0·0438	0·0383	0·0346	0·0273	0·0279	0·0253	0·0244	0·0237	0·0228	0·0227
Penna H_3 (V.I. = 100). 140 Saybolt at 210° F.	1,670	776	398	223	134	85·5	57·2	39·9	28·8	0·0820	0·0695	0·0590	0·0515	0·0450	0·0399	0·0356	0·0283	0·0267	0·0251	0·0242	0·0233	0·0227	0·0222
Coastal L_1 (V.I. = 0). 80 Saybolt at 210° F.	1,890	694	302	150	82·9	49·7	31·8	21·5	15·2	0·1145	0·0900	0·0730	0·0605	0·0515	0·04435	0·0386	0·0403	0·0363	0·0336	0·0315	0·0304	0·0296	0·0290
Coastal L_2 (V.I. = 0). 120 Saybolt at 210° F.	5,670	1,800	694	315	161	90·8	55·2	35·7	24·3	0·138	0·107	0·0845	0·0695	0·0582	0·0499	0·0433	0·0424	0·0377	0·0338	0·0315	0·0297	0·0287	0·0279
Coastal L_3 (V.I. = 0). 140 Saybolt at 210° F.	8,460	2,510	932	409	204	112	67·8	42·5	28·5	0·150	0·1127	0·0890	0·0728	0·0608	0·0512	0·0463	0·0441	0·0380	0·0341	0·0315	0·0297	0·0280	0·0285

Index " of Dean and Davis,[17] but is distinguished by the fact that it is not based on any arbitrarily chosen series of oils. In a later paper it is hoped to extend this discussion to the derivation of an expression better adapted for the classification of lubricating-oil hydrocarbons and for the correlation of chemical structure with temperature coefficient of viscosity.

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SPARK PHOTOGRAPHY OF FUEL SPRAYS, AND HIGH-SPEED MOTION PICTURE STUDY OF COMBUSTION IN A COMPRESSION IGNITION ENGINE.*

RESEARCH on the behaviour of fuel sprays has been in progress for many years at the Langley Memorial Aeronautical Laboratory under the direction of the National Advisory Committee for Aeronautics, and the following is an abstract of four of the more recent papers which are of particular interest.

These are :—

" Experiments on Distribution of Fuel in Fuel Sprays." T.R. No. 438. D. W. Lee. 1932.

" A Preliminary Motion-Picture Study of Combustion in a Compression Ignition Engine." T.N. No. 496. E. C. Buckley and C. D. Waldron. 1934.

" A Comparison of Fuel Sprays from Several Types of Injection Nozzles." T.R. No. 520. D. W. Lee. 1935.

" Some Effects of Injection Advance Angle, Engine Jacket Temperature and Speed on Combustion in a Compression Ignition Engine." T.R. No. 525. A. M. Rothrock and C. D. Waldron. 1935.

APPARATUS AND TECHNIQUE.

Three major methods of examination of fuel sprays have been developed. The study of sprays into the atmosphere, compressed air and transparent liquids has been made with the aid of photography depending on illumination of the spray by spark discharges from a batch of charged condensers. Early tests were made with the sparks persisting for periods varying from 0·00001 to 0·000001 sec., but this was found to be too long for analysis of the finer details of spray structure. An alteration to the circuit enabled exposures of an estimated duration of only 0·0000001 sec. to be obtained.

Photomicrographs have been taken to show the stages in the breakdown of a fuel jet.

In addition to photographic methods, a study has been made of the penetrative power of different sprays, and of different parts of the same spray, by directing the discharge into Plasticine blocks.

A special engine, firing only for one cycle, has been built for the study of combustion, indicator diagrams of the pressure changes being taken with an optical indicator of the diaphragm type, and photographs of the actual combustion with a special motion-picture camera. One wall of the combustion chamber carried a double window, through which the photographs were taken, the image being focussed on the moving film by an

* Abstract by R. Stansfield of four papers published by the National Advisory Committee for Aeronautics, U.S.A.

optical system which included a rotating prism. In this way the image was made to follow the film movement, and exposures were possible at speeds up to 2500 frames per sec.

In the records described, the taking speed was 2500 frames per sec., with an exposure time of one-third of the intervals between successive exposures. This represents an image covering about two degrees of crankshaft rotation at 570 r.p.m.

Photography of the sprays themselves in the engine was effected by fitting double windows at opposite sides of the combustion chamber (the diaphragm indicator then being removed), a piece of ground glass being interposed between one pair of windows and giving an even illumination having its source in an arc light. The spray then appeared as a dark silhouette, and the combustion, brighter than the illumination from the arc, stood out in sharp contrast.

Summary of Results.

Formation of Fuel Sprays.—The density of the air into which fuel is injected has little effect on the ultimate fineness of atomization, but increase of air density causes the atomizing to take place nearer to the nozzle. The breakdown of the fuel jet is due, primarily, to air friction, the jet first being torn into ligaments, and these being rapidly transformed into drops by the surface tension of the fuel. Under practical conditions a fuel drop never penetrates *by its own energy* more than one inch into the combustion chamber, but much greater penetration may occur, because the central part of the spray gives a forward velocity to the air ahead and the drops move relatively to this air blast. The central core travels faster than the envelope, fuel particles being continually torn aside from the core, which is moving rapidly in relation to the air ahead, and being forced aside as they give momentum to the air and lose their own high initial velocity.

Fig. 1 shows photomicrographs of the various stages in the breakdown of a fuel spray injected into air at atmospheric pressure.

The core of a spray from a plain nozzle becomes larger in diameter during the early part of its movement from the nozzle, but as the fuel is torn away the diameter decreases again. Comparison of spray photographs and spray impressions made in Plasticine from the same nozzle, injecting at 4000 lb. per sq. in. into air at a density of 1·1 lb. per c. ft., showed that the spray envelope had a diameter about three times the core diameter for a distance up to about 2 inches from the nozzle, this ratio increasing to about nine times at 3 inches, and the jet having no penetrative force left at 4 inches.

Air jets directed at a velocity of the order of 60 ft. per sec. against the side of the fuel spray had no effect on the core. An air velocity of about 300 ft. per sec. was needed to affect the core during the injection period.

The distribution of the fuel, both in the core and in the envelope, is very uneven, both being divided into particles under engine operating conditions by the time the fuel has penetrated 0·75 inch.

The core becomes shorter and thicker as the density of the air in the combustion chamber increases.

Fineness of atomization increases with fuel injection velocity and with decrease of orifice diameter, but not to any great extent with length-diameter ratio nor air density.

Many other nozzle types were tested, including impinging jets, pintle nozzles with full and limited lift, multiple orifice, slit and centrifugal nozzles. An interesting feature of the behaviour of the pintle nozzle was the change in the type of spray core with the amount of lift, although the variation was only slight under engine conditions of air density, in contrast with an extreme variation when spraying into air at atmospheric pressure.

Fig. 2 shows photographs of various types of spray from different injection nozzles. The distribution of fuel in these sprays can only be determined in conjunction with records of core penetration into Plasticine or, more delicately, by the methods developed by P. H. Schweitzer.

Combustion in the Engine.—Motion-picture photography at a speed of 2500 frames per sec. showed that when combustion started during the period of lift of the spray valve the ignition began in the spray envelope, and usually at several points.

When the delay time of the fuel was such that the spray valve had closed before burning started, the ignition might begin anywhere in the combustion space. Under conditions of test the rate of burning increased and the total time of burning decreased as the injection timing was advanced from 0 to 40 degrees before top centre. When the running conditions were smooth the progress of burning could be followed with reasonable completeness, but when knocking occurred the flame spread so rapidly as to fill almost the entire combustion chamber between successive photographs 1/2500 sec. apart. It should be mentioned that the combustion chamber was of the open type, with only the moderate and indiscriminate turbulence produced by the ejection of air into the chamber, as the piston crown nearly reached the crown of the cylinder proper.

When the delay time was relatively short, the ignition, starting at several points in the spray envelope, developed in about 2 degrees to larger areas of connected flames with irregular edges, and in a further 2 degrees to a flame completely filling the combustion chamber. The maximum pressure was not reached until several degrees later, and the flame filled the combustion space until more than 20 degrees after top centre. It then became smaller, and after the 90 degree point only a few isolated and small flames existed.

When injection was advanced, the delay was increased and more isolated areas of flame appeared before the burning became general, although the flame travel rate was greater once the spread took place. The pressure rise was still not sufficiently rapid to cause knock, and there was some after-burning, which appeared to be from masses of burning gas, in contrast with burning nuclei noticed during the combustion photographs taken with the late start of injection.

With still earlier injection, 40 degrees before top centre, the pressure indicator showed that the rate of burning was very rapid. The flame started in only two isolated places, but had spread throughout the combustion chamber in a further two degrees. The actual rate of heat input to the air decreased, and the flame distribution indicated that the fuel was

FIG. 1.

PHOTOMICROGRAPHS SHOWING VARIOUS STAGES IN THE BREAKDOWN OF A LOW-VELOCITY FUEL JET, × 10. (REDUCED TO FOUR-FIFTHS LINEAR IN REPRODUCTION.) INJECTION PRESSURE, 100 LB. PER SQ. IN.; AIR DENSITY, 1 ATM.; DIAMETER OF DISCHARGE ORIFICE, 0·020 INCH.

[*To face p.* 330.

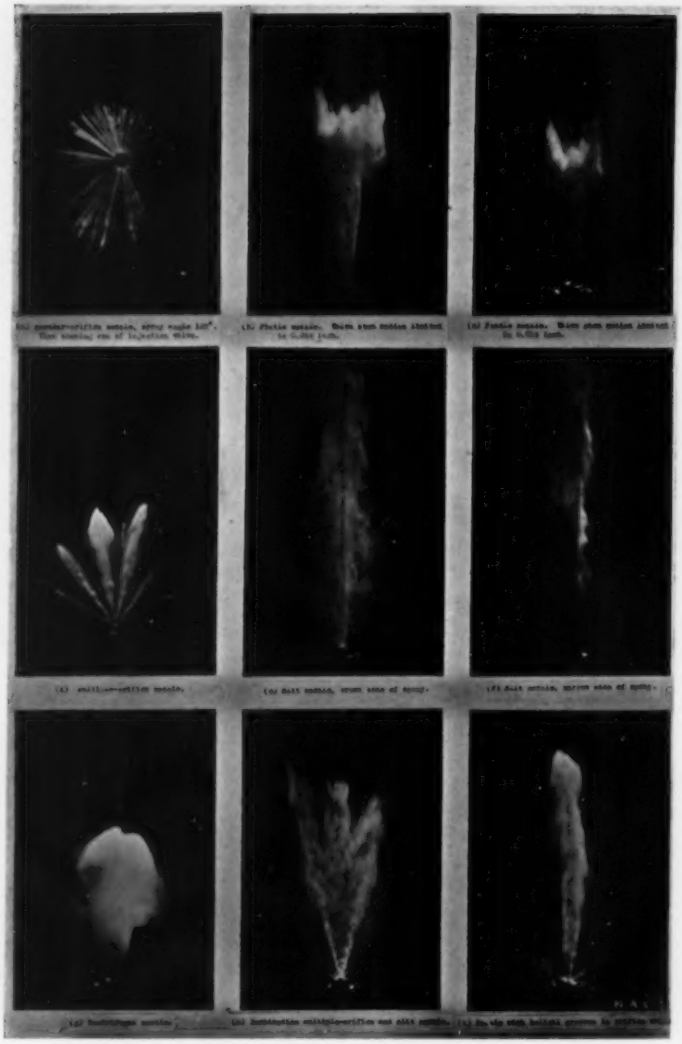

FIG. 2.

PHOTOGRAPHS OF THE EARLY STAGES OF SPRAYS FROM THE NOZZLES TESTED. INJECTION PRESSURE, 4000 LB. PER SQ. IN.; AIR DENSITY, 1 ATM.

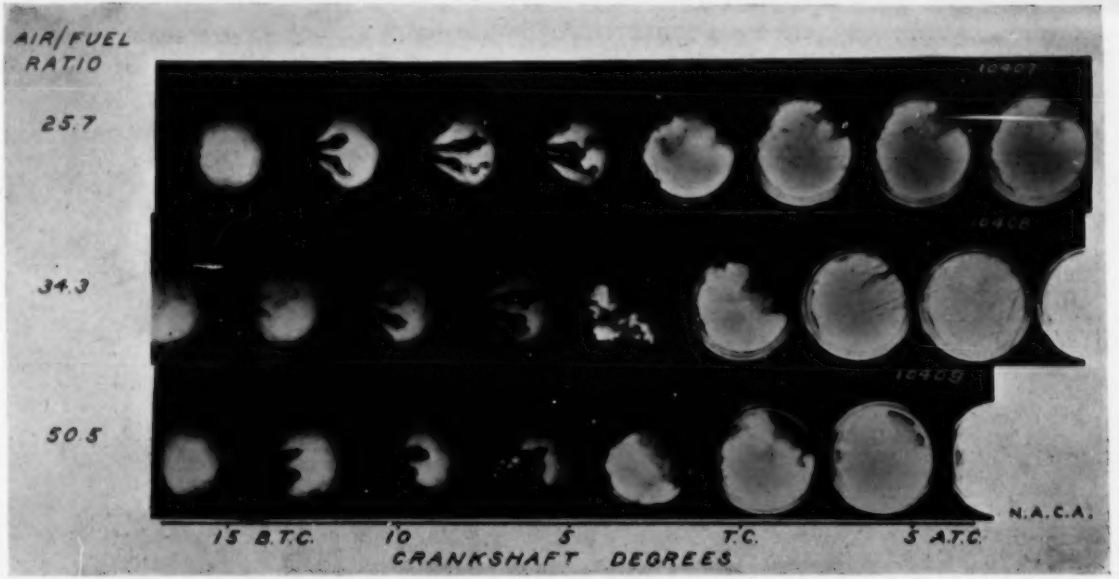

FIG. 3.

EFFECT OF AIR-FUEL RATIO ON FUEL SPRAY AND FLAME FORMATION. ENGINE SPEED, 1500 R.P.M.; JACKET TEMPERATURE, 150° F.

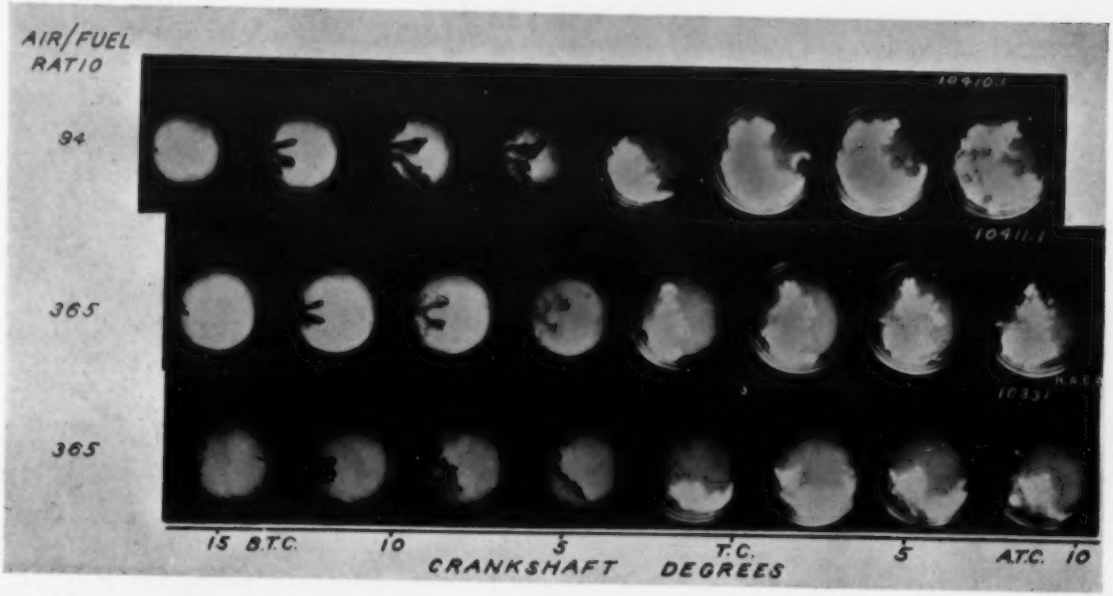

FIG. 4.

EFFECT OF AIR-FUEL RATIO ON FUEL SPRAY AND FLAME FORMATION. ENGINE SPEED, 1500 R.P.M.; JACKET TEMPERATURE, 150° F.

not forming a homogeneous mass with the air. The total duration of burning decreased as the timing was advanced.

Later tests were made at engine speeds of 570 and 1500 r.p.m., with the engine-jacket temperature varied from 100° F. to 300° F. and the injection advance angle from 13° after to 120° before top centre. The conclusion is reached that the course of combustion is controlled largely by the temperature and pressure of the air between the moment of beginning of injection and the time at which combustion starts.

It is also suggested that, in an engine with a *quiescent* combustion chamber, the ignition lag should be sufficiently small to avoid excessive rise of pressure, but that further shortening decreases the effective combustion. The latter conclusion is based on results obtained by heating the air charge, thus making it more difficult for a given fuel droplet to reach the oxygen supply necessary for its burning. It may or may not apply to the effect of change of ignition quality of fuel under constant conditions of air temperature, even with a quiescent combustion chamber, nor is it necessarily applicable to an engine where there is deliberate introduction of turbulence for the purpose of obtaining good mixing of fuel particles and air.

Figs. 3 and 4 are combustion photographs taken at 1500 r.p.m. with various air/fuel ratios. In the earlier frames of each series the shadow of the spray envelope is clearly visible, and in most cases the beginning of combustion can be detected at several points in the envelope. It will be noticed that there was no substantial difference between the delay times at the end of which the flame had become established over the entire range of air/fuel ratios from 365 to 25·7 : 1.

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THE PHYSICAL CONSTANTS OF POLYMERIZATION PRODUCTS OF UNSATURATED HYDROCARBONS.*

By H. I. Waterman, J. J. Leendertse and J. Ph. Makkink.

In recent years several unsaturated hydrocarbons have been polymerized. The products of the reaction have been analysed using the specific refraction after complete hydrogenation, in connection with the mean molecular weight as a measure for the nature of the products.[1] Thus polymerization products have been analysed obtained from *n*-2-pentene with aluminium chloride as a catalyst at about 0° C.,[2] and from isobutene with aluminium oxide on silica gel as a catalyst at a maximum temperature of 40° C.[3] These products were used for an investigation in which the authors have begun to study the relation between the chemical nature of hydrocarbon mixtures and their viscosities and viscosity–temperature curves.[4] The viscosities were determined in c.g.s. units.

In using several *series* of polymerization products consisting of polymer fractions with gradually increasing molecular weight, mistakes in the results by accidental impurities may be eliminated, and the influence of the molecular weight on the viscosity and viscosity–temperature curve can be shown. The olefines chosen as the raw material for the various series differed not only in molecular weight, but also in structure. In the future the results of these investigations may be useful in predicting physical constants, such as the viscosity and the viscosity–temperature curve, from other physical constants which can easily be determined. Thus the authors intend to develop a method for predicting constants of important technical significance from other physical constants, of which the determination is very simple.

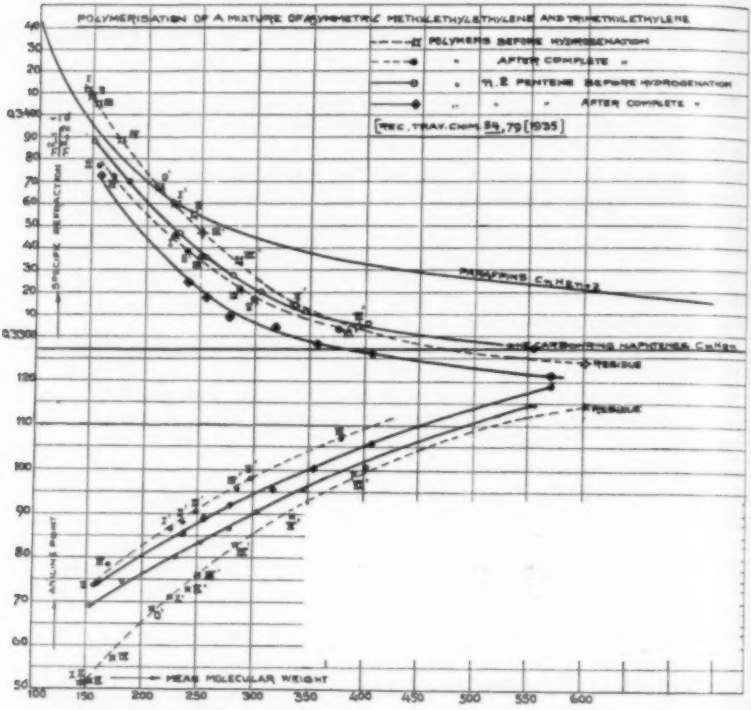
The authors have now examined a series of polymer fractions obtained from a mixture of *branched* pentenes (a mixture of asymmetric methylethylethylene and trimethylethylene) and compared with the *unbranched* 2-pentene polymers. The branched pentenes were obtained by dehydrating tertiary amyl alcohol over aluminium oxide at 400° C. The conditions in the polymerization were analogous with the conditions in the *n*-2-pentene polymerization previously described (temperature about 0° C., aluminium chloride as a catalyst). The total reaction product was analysed,[1] after separating it into several fractions. The results of the analysis may be read from Fig. 1. Also the normal 2-pentene polymer fractions have been indicated in the figure. Thus it may be seen that the polymers last mentioned are more cyclic in character, although the differences are very small.

As to the quantities of the several fractions obtained from the branched pentenes, the dimer fraction includes about 20 to 25 per cent. of the total reaction product, the quantities of the other fractions being smaller (about 6 to 8 per cent.).

* Paper received January 8th, 1936.

Method of Determining the Viscosity.

The majority of the viscosity determinations were done at 20°, 40°, 60° and 80° C. before and after hydrogenation, with the Wi. Ostwald type of viscosimeter. The experiments were carried out according to the instruc-



Fraction.	Fractions before Hydrogenation. $n_D^{t°}$.	$d_4^{t°}$.	A.P. °C.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$.	Mean Molecular Weight (C_5H_8).	Fractions after Complete Hydrogenation. $n_D^{t°}$.	$d_4^{t°}$.	A.P. °C.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$.	Mean Molecular Weight (C_5H_8).
I . .	1·4338	0·7633	51·5	0·3411	143	—	—	—	—	—
II . .	1·4348	0·7653	51·7	0·3408	148	1·4210	0·7504	73·4	0·3379	155
III .	1·4370	0·7694	52·2	0·3405	154	—	—	—	—	—
IV .	1·4420	0·7808	57·1	0·3389	174	1·4263	0·7602	78·4	0·3373	172
0′ . .	1·4498	0·7977	68·7	0·3368	209	—	—	—	—	—
I′ . .	1·4533	0·8050	71·2	0·3359	225	1·4415	0·7900	86·4	0·33465	225
II′ . .	1·4551	0·8087	72·6	0·3356	241	1·4438	0·7955	87·9	0·3338	236
III′ .	1·4576	0·8147	75·8	0·3347	250	1·4455	0·7986	90·3	0·3336	250
IV′ .	1·4614	0·8237	82·8	0·3334	283	1·4524	0·8127	95·6	0·3322	284
V′ .	1·4645	0·8336	88·8	0·3313	334	1·4528	0·8142	98·2	0·3318	297
VI′ .	1·4682	0·8417	99·0	0·3304	390	1·4617	0·8313	107·4	0·3305	379
Residue.	1·4765	0·8585	114·8	0·3288	601	—	—	—	—	—
B. Oil .	1·4682	0·8488	70·9	0·3276	305	—	—	—	—	—

Fig. 1.

tions of the British Standards Institution.[5] In the cases where the time of flow was less than 100 seconds, the kinetic energy correction was applied.

The results of the experiments are given in Table I, where may be read the number of the viscometer used, the time of flow in seconds, the density of the liquid at the temperature of the determination (corrected for buoyancy), the viscosity in centipoises and in centistokes, and the logarithm of the viscosity in poises and in stokes.

The formulæ for the calculation of the viscosity, belonging to the viscometer number given in Table I, may be read from Table II.

In Table III also, the kinetic values of the viscosity (in centistokes) and the logarithm of the viscosity (in stokes) for the normal 2-pentene- and the isobutene polymers [4] are given.

Discussion of the Results.

The viscosity of the polymerization products obtained in this case increases from a very low value to a value that approaches the viscosity of light lubricating oils.

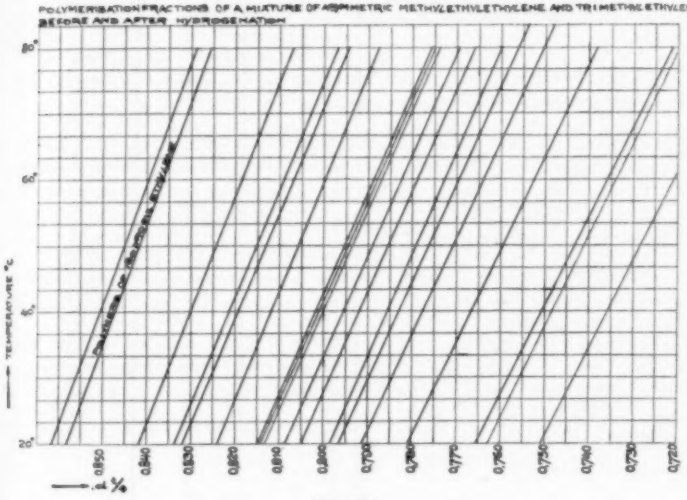


Fig. 2.

The results can be read graphically. Several values for the *iso*butene- and *n*-2-pentene polymers (compare the previous paper) are also indicated in the graphs.

Fig. 2. For each polymer fraction the relation between the *density* (d_4^t) and the *temperature* (° C.) is a linear one, at least for temperatures from 20° to 80° C. The influence of the temperature on the density decreases with increasing molecular weight of the fractions.

Fig. 3 indicates, for all polymer fractions before and after hydrogenation, the *log. viscosity* (in poises)–*temperature* (° C.) curve. The influence

of the temperature on the viscosity increases regularly with increasing molecular weight of the fractions.

In Fig. 4 for several fractions the relation between $\log \phi = -\log \eta_{abs.}$

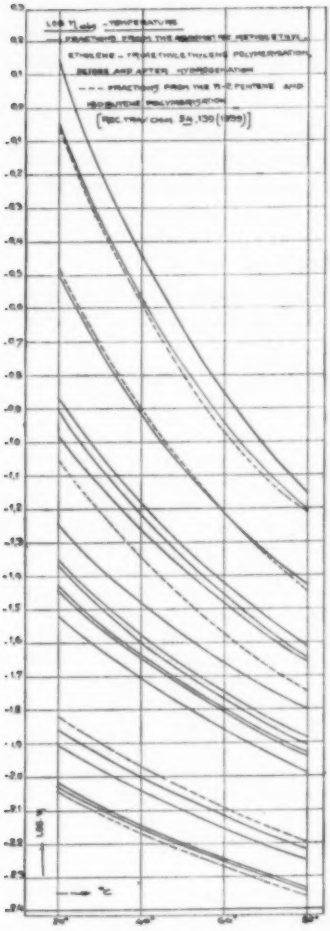


FIG. 3.

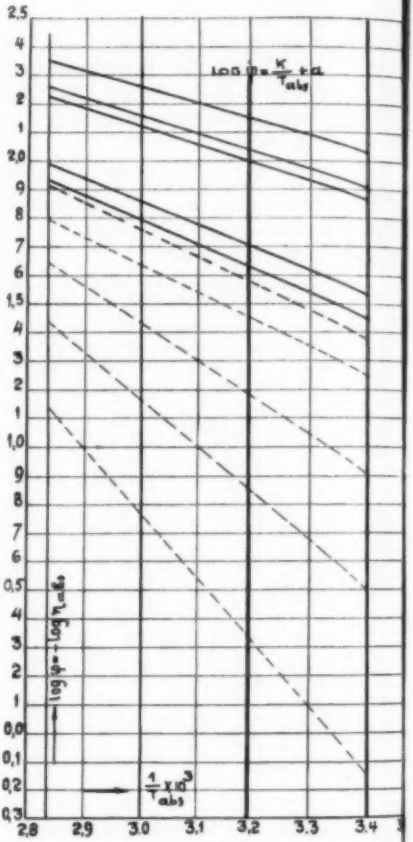


FIG. 4.

(η in poises) and $\frac{1}{T}$ is given (T is the temperature in ° K.). The low molecular fractions indicate a linear relationship; in increasing the molecular weight the deviations from the linear curve increase.

Fig. 5. Using the relation mentioned in the case of Fig. 4, Fig. 5 has been constructed to obtain a certain number which is a measure for the

slope of the viscosity–temperature curve, belonging to the viscosity at a definite temperature, in this case 20° C. Fig. 5 represents the relation between $\frac{\log \phi_{80} - \log \phi_{20}}{\frac{1}{T_{20}} - \frac{1}{T_{80}}}$ and $\log \phi_{20}$ for the fractions. ϕ is derived from η in poises.

Fig. 6 is an analogous graph; in this case the kinetic value of the viscosities has been used.

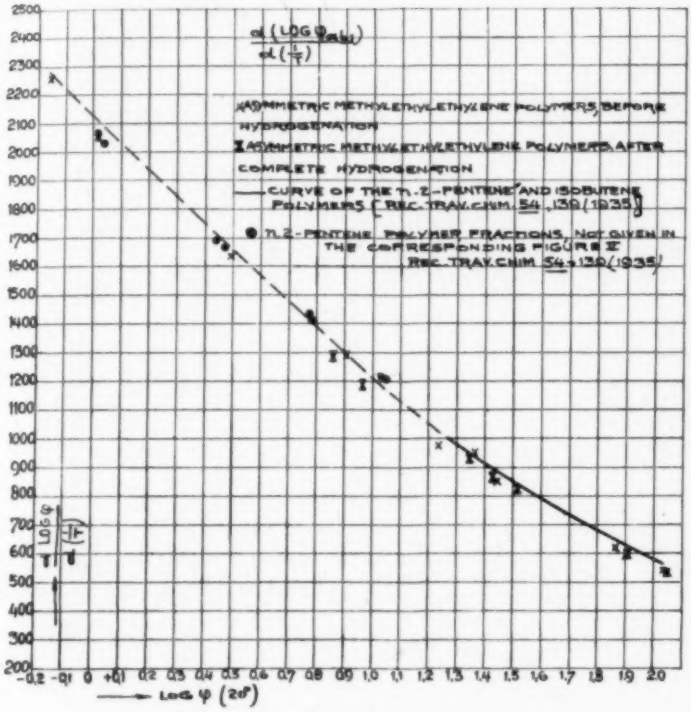

ASYMMETRIC METHYLETHYLETHYLENE POLYMERS, BEFORE HYDROGENATION
ASYMMETRIC METHYLETHYLETHYLENE POLYMERS, AFTER COMPLETE HYDROGENATION
CURVE OF THE TR.-2-PENTENE AND ISOBUTENE POLYMERS (REC. TRAV. CHIM. 54, 130 (1935))
TR.-2-PENTENE POLYMER FRACTIONS, NOT GIVEN IN THE CORRESPONDING FIGURE Σ REC. TRAV. CHIM. 54, 130 (1935)
LOG φ (20°)

FIG. 5.

To a certain extent this relationship between kinetic viscosities is comparable with results obtained from technical viscometers, *e.g.* the Saybolt Universal viscometer.

In Figs. 7*a* and 7*b*, the viscosity at $t°$ C. is represented horizontally, the corresponding viscosity value for the same fraction at the temperature $t + 20°$ C. vertically. It has been proved that *one* curve represents the values for all the polymer fractions at 20°, 40°, 60° and 80° C. From these graphs, and also partly from the Figs. 5 and 6, it is possible to deduce the viscosity at several temperatures if we know the viscosity of the fractions at one temperature.

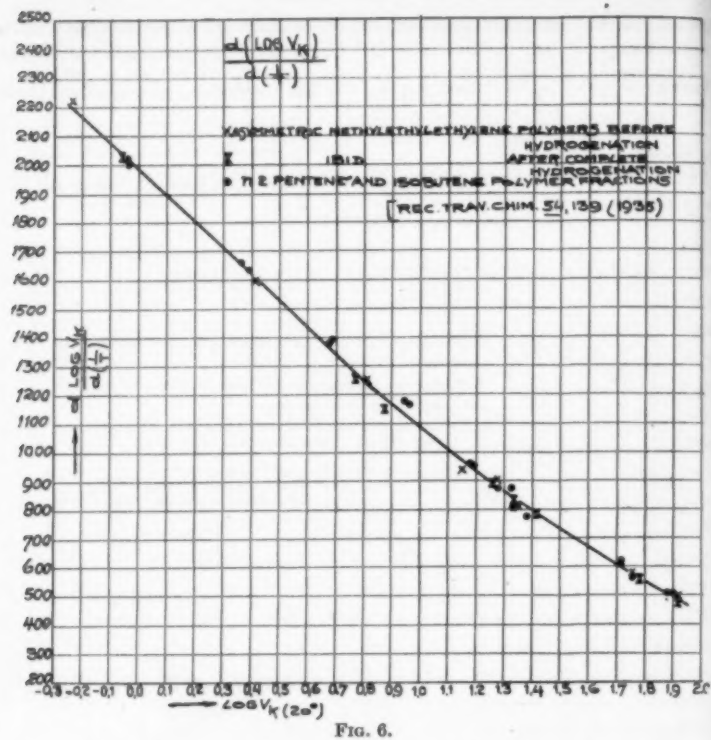

ASYMMETRIC METHYLETHYLETHYLENE POLYMERS BEFORE HYDROGENATION
AFTER COMPLETE HYDROGENATION
I.B.I.D.
TRI 2 PENTENE AND ISOBUTENE POLYMER FRACTIONS
[REC. TRAV. CHIM. 54, 139 (1935)]
LOG V_K (20°)

FIG. 6.

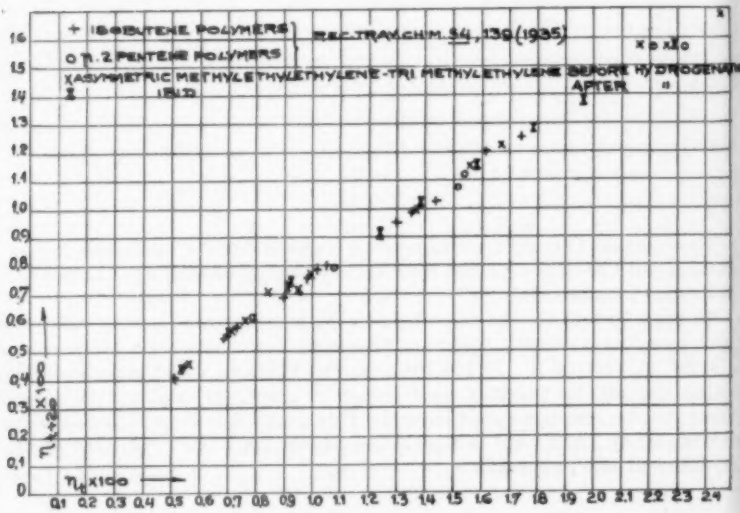

+ ISOBUTENE POLYMERS
O TRI 2 PENTENE POLYMERS
REC. TRAV. CHIM. 54, 139 (1935)
ASYMMETRIC METHYLETHYLETHYLENE-TRI METHYLETHYLENE BEFORE HYDROGENATION
AFTER
I.B.I.D.
$\eta_k \times 100$

FIG. 7a.

Fraction number.		Mean Molecular Weight (C_6H_6).	20°.								
			Visc. number.	Time of Flow (secs.).	$d_4^{20°}$.	$\eta_{abs.}$ (centipoises)	log $\eta_{abs.}$ (poises)	$V_{k\,(centistokes)}$	log $V_{k\,(stokes)}$	Visc. number.	Time Flo (secs
II	Before hydrogenation	148	1*b*	140·1	0·7655	0·936	−2·029	1·225	−1·912	1*b*	108
IV		174	1*b*	200·9	0·7808	1·369	−1·864	1·756	−1·756	1*b*	148
I′		225	2*b*	78·2	0·8050	3·585	−1·445	4·461	−1·351	1*b*	327
II′		241	2*b*	93·2	0·8087	4·297	−1·367	5·321	−1·274	1*b*	354
III′		250	2*b*	123·7	0·8147	5·768	−1·239	7·091	−1·149	2*b*	71
IV′		283	2*b*	266·4	0·8237	12·57	−0·901	15·28	−0·816	2*b*	128
V′		334	3*d*	143·1	0·8336	31·96	−0·495	38·39	−0·416	2*b*	256
VI′		390	3*d*	631·3	0·8417	142·3	+0·1534	169·3	+0·229	3*d*	163
II	After hydrogenation	155	1*d*	133·8	0·7511	0·915	−2·038	1·220	−1·914	1*d*	104
IV		172	1*d*	178·6	0·7611	1·238	−1·907	1·629	−1·788	1*d*	134
I′		225	1*d*	422·0	0·7912	3·039	−1·517	3·849	−1·415	1*d*	277
II′		236	1*d*	509·8	0·7962	3·694	−1·432	4·646	−1·333	1*d*	321
III′		250	1*d*	614·8	0·7982	4·469	−1·350	5·607	−1·251	1*d*	372
IV′		284	2*d*	232·6	0·8130	10·83	−0·965	13·36	−0·874	2*d*	117
V′		297	2*d*	296·3	0·8142	13·82	−0·859	17·00	−0·769	2*d*	142
VI′		379	3*c*	370·7	0·8318	95·21	−0·021	114·7	+0·059	3*c*	108

TABLE II.

Viscosimeter number.	$t > 100$ sec.	$t < 100$ sec.	Range.[a]
1*b*	$\eta_{(cp.)} = 0{\cdot}00874\rho t$	$\eta_{(cp.)} = 0{\cdot}00874\rho t - \frac{0{\cdot}5\rho}{t}$	0·9–7·2 cp.
1*d*	$\eta_{(cp.)} = 0{\cdot}00912\rho t$	$\eta_{(cp.)} = 0{\cdot}00912\rho t - \frac{0{\cdot}5\rho}{t}$	0·9–7·2 cp.
2*b*	$\eta_{(cp.)} = 0{\cdot}05732\rho t$	$\eta_{(cp.)} = 0{\cdot}05732\rho t - \frac{2{\cdot}1\rho}{t}$	5·4–43 cp.
2*d*	$\eta_{(cp.)} = 0{\cdot}0574\rho t$	—	5·4–43 cp.
3*c*	$\eta_{(cp.)} = 0{\cdot}3092\rho t$	—	32–260 cp.
3*d*	$\eta_{(cp.)} = 0{\cdot}2683\rho t$	—	32–260 cp.

η = viscosity; ρ = density at the temperature of determination of the viscosity (uncorrected); t = time of flow (seconds).

[*To face p.* 238.

TABLE I.

	40°.							60°.							80°.						
	Visc. number.	Time of Flow (secs.).	$d_4^{t°}$.	$\eta_{abs.}$ (centipoises)	log $\eta_{abs.}$ (poises)	V_k (centistokes)	log $V_{k\,(stokes)}$	Visc. number.	Time of Flow (secs.).	$d_4^{t°}$.	$\eta_{abs.}$ (centipoises)	log $\eta_{abs.}$ (poises)	V_k (centistokes)	log $V_{k\,(stokes)}$	Visc. number.	Time of Flow (secs.).	$d_4^{t°}$.	$\eta_{abs.}$ (centipoises)	log $\eta_{abs.}$ (poises)	V_k (centistokes)	log $V_{k\,(stokes)}$
2	1*b*	108·5	0·7505	0·711	−2·148	0·948	−2·023	1*b*	87·7	0·7364	0·559	−2·252	0·761	−2·118	1*b*	73·3	0·7209	0·456	−2·341	0·634	−2·198
6	1*b*	148·5	0·7668	0·994	−2·003	1·298	−1·887	1*b*	115·6	0·7524	0·759	−2·120	1·010	−1·996	1*b*	93·4	0·7381	0·598	−2·224	0·811	−2·091
1	1*b*	327·0	0·7922	2·260	−1·646	2·858	−1·544	1*b*	229·7	0·7789	1·562	−1·806	2·007	−1·697	1*b*	172·6	0·7658	1·153	−1·938	1·509	−1·821
4	1*b*	354·0	0·7956	2·458	−1·609	3·094	−1·509	1*b*	245·4	0·7824	1·676	−1·776	2·145	−1·669	1*b*	181·2	0·7697	1·217	−1·915	1·584	−1·800
9	2*b*	71·4	0·8015	3·253	−1·488	4·064	−1·391	1*b*	314·8	0·7887	2·167	−1·664	2·751	−1·560	1*b*	232·1	0·7759	1·571	−1·804	2·029	−1·693
6	2*b*	128·5	0·8118	5·971	−1·224	7·367	−1·133	2*b*	76·6	0·7998	3·485	−1·458	4·365	−1·360	1*b*	325·8	0·7874	2·239	−1·650	2·847	−1·545
6	2*b*	256·3	0·8227	12·07	−0·918	14·69	−0·833	2*b*	131·4	0·8090	6·085	−1·216	7·534	−1·123	2*b*	79·6	0·7981	3·617	−1·442	4·538	−1·343
9	3*d*	163·5	0·8300	36·35	−0·439	43·86	−0·358	2*b*	297·6	0·8187	13·95	−0·855	17·06	−0·768	2*b*	151·5	0·8066	6·995	−1·155	8·686	−1·061
4	1*d*	104·73	0·7361	0·702	−2·154	0·955	−2·020	1*d*	84·93	0·7211	0·554	−2·257	0·768	−2·115	1*d*	70·67	0·7058	0·449	−2·348	0·637	−2·196
8	1*d*	134·13	0·7487	0·914	−2·039	1·223	−1·912	1*d*	104·8	0·7345	0·701	−2·154	0·956	−2·020	1*d*	86·00	0·7198	0·559	−2·252	0·778	−2·109
5	1*d*	277·33	0·7776	1·963	−1·707	2·529	−1·597	1*d*	198·80	0·7636	1·383	−1·859	1·813	−1·742	1*d*	149·07	0·7503	1·018	−1·992	1·360	−1·867
3	1*d*	321·27	0·7831	2·292	−1·640	2·930	−1·533	1*d*	225·07	0·7699	1·578	−1·802	2·053	−1·688	1*d*	168·47	0·7561	1·160	−1·936	1·537	−1·814
1	1*d*	372·87	0·7856	2·667	−1·574	3·401	−1·468	1*d*	255·27	0·7732	1·797	−1·745	2·328	−1·633	1*d*	186·53	0·7594	1·290	−1·889	1·701	−1·769
4	2*d*	117·3	0·8000	5·378	−1·269	6·733	−1·172	1*d*	475·1	0·7873	3·406	−1·468	4·333	−1·363	1*d*	316·5	0·7740	2·230	−1·652	2·887	−1·540
9	2*d*	142·8	0·8013	6·558	−1·183	8·196	−1·086	1*d*	527·1	0·7889	3·787	−1·422	4·807	−1·318	1*d*	350·6	0·7761	2·477	−1·606	3·198	−1·495
0	3*c*	108·7	0·8191	27·50	−0·561	33·62	−0·473	2*d*	254·5	0·8073	11·78	−0·929	14·61	−0·835	2*d*	134·0	0·7943	6·101	−1·215	7·691	−1·114

TABLE III.

Fraction.	20°.		80°.		$\frac{d \log V_k}{d \frac{1}{T}}$.
	$V_{kin.\,(centistokes)}$.	log $V_{kin.\,(stokes)}$.	$V_{kin.\,(centistokes)}$.	log $V_{kin.\,(stokes)}$.	
n-2-*Pentene polymers*					
20–40° C. (3 mm.) before hydrogenation . .	1·229	−1·910	0·625	−2·204	507
20–40° C. (3 mm.) after ,, . .	1·242	−1·906	0·629	−2·202	510
40–55° C. (3 mm.) before ,, . .	1·947	−1·711	0·847	−2·072	622
C.V.D.I.C. vapour 35–57° before hydrogenation .	4·196	−1·377	1·483	−1·829	779
,, ,, 35–57° after ,, .	4·755	−1·323	1·473	−1·832	878
,, ,, 57–63° before ,, .	6·397	−1·194	1·780	−1·749	957
,, ,, 57–63° after ,, .	6·551	−1·184	1·811	−1·742	962
,, ,, 63–66° before ,, .	10·92	−0·962	2·285	−1·641	1171
,, ,, 63–66° after ,, .	11·11	−0·954	2·303	−1·638	1179
,, ,, 66–76° before ,, .	20·30	−0·693	3·125	−1·505	1400
,, ,, 66–76° after ,, .	20·50	−0·688	3·199	−1·495	1391
,, ,, 76–93° before ,, .	39·93	−0·399	4·459	−1·351	1641
,, ,, 76–93° after ,, .	42·80	−0·369	4·660	−1·332	1660
,, ,, 93–110° before ,, .	108·1	+0·034	7·591	−1·120	1990
,, ,, 93–110° after ,, .	111·8	+0·0482	7·450	−1·128	2028
Isobutene polymers fraction with					
Molecular weight **114** before hydrogenation .	0·743	−2·129	0·429	−2·368	412
,, ,, **119** after ,, .	0·750	−2·125	0·435	−2·362	409
,, ,, **147** before ,, .	1·283	−1·892	0·644	−2·191	516
,, ,, **151** after ,, .	1·239	−1·907	0·641	−2·193	493
,, ,, **173** before ,, .	1·914	−1·718	0·847	−2·072	610
,, ,, **178** after ,, .	1·747	−1·758	0·827	−2·083	560
,, ,, **175** before ,, .	1·973	−1·705	0·868	−2·061	614
,, ,, **181** after ,, .	1·823	−1·739	0·848	−2·072	574
,, ,, **234** before ,, .	5·342	−1·272	1·663	−1·779	874
,, ,, **228** after ,, .	4·720	−1·326	1·613	−1·792	803

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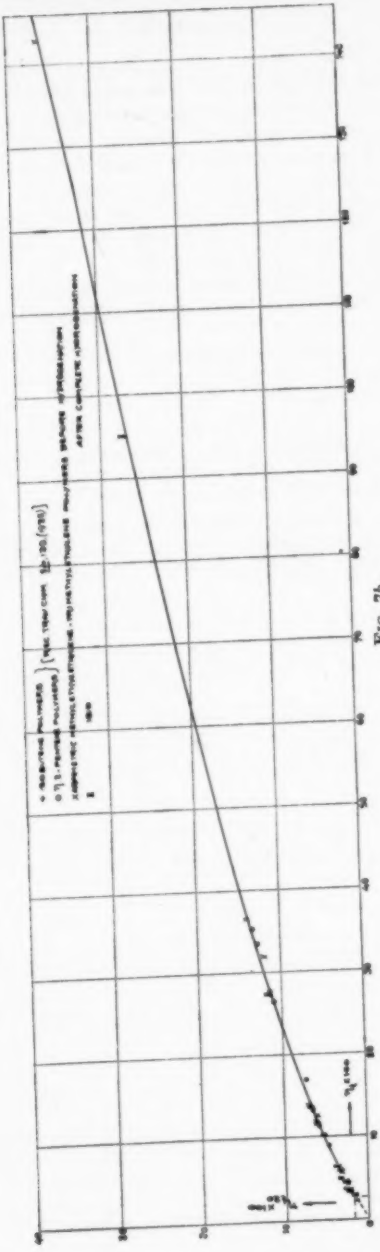

FIG. 7b.

Conclusion.

From the graphs it may be seen that in the case of the normal 2-pentene and the asymmetric methylethylethylene–trimethylethylene mixture the viscosity properties of the polymerization fractions are independent of the chemical structure of the pentenes used in the polymerization. The ramification of the pentenes in this case has no influence on the viscosity properties of the polymers obtained under analogous conditions. However, it must be remarked that the method used in comparing the viscosity-temperature curves is not a sensitive one. It is suitable for detecting more important differences in the products.

Afterwards smaller differences must be examined in another way. The authors intend to enlarge these investigations in several directions.

Delft, Laboratory of Chemical Engineering.
September 1935.

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[2] H. I. Waterman, J. J. Leendertse, and W. M. Klazinga, *Rec. trav. chim.*, 1935, **54**, 79.
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[5] British Standard Method (No. 188—1929) for the determination of viscosity in absolute units, London, 1929.

DESULPHURIZATION OF HYDROCARBONS WITH CARBON MONOXIDE.*

By Boris W. Malishev.

This work was undertaken with the object of studying the desulphurization of hydrocarbons with carbon monoxide in presence of catalysts. This method is analogous to desulphurization by hydrogenation, and would be operative with some of the catalysts used in the latter process. The sulphur would be removed as carbon oxy-sulphide (COS) similarly to removal of sulphur as H_2S in hydrogenation.

A number of catalysts were tried first in a rotating autoclave of 100 c.c. capacity at a temperature of 300° C., and at a pressure of 1000 lb. per sq. inch of carbon monoxide in order to establish their comparative efficiency. These catalysts were: Ni, NiS, Cu, Te, Pd, CoS and MoS_3. From all these catalysts, MoS_3 gave the highest sulphur reduction. Nickel and NiS reduced the sulphur content of a pressure distillate only from 0·98 per cent. to 0·82 per cent. The reaction was complicated by formation of large quantities of nickel carbonyl. Copper and tellurium were without any effect, and also the mineral molybdenite. Palladium on asbestos reduced the sulphur content of a solution of thiophene in toluene from 0·78 per cent. to 0·67 per cent.

As the effect of the catalysts largely depends on the method of their preparation and as the mechanism of the desulphurization reaction with CO is not completely clear, the classification of the catalysts for their efficiency would be premature.

It has been shown in this investigation that the organic sulphur is removed as COS. Stock, Sieke and Pohland [1] studied the reaction between S and CO, and found that the equilibria is determined by the following reactions:

$$COS \rightleftarrows CO + S \text{ and } 2COS \rightleftarrows CO_2 + CS_2.$$

The quantities present in the equilibrium mixture at atmospheric pressure are as follows:

Table I.

The COS *Equilibrium.*

(All percentage figures represent COS present or decomposed).

Temperature .	100° C.	200° C.	300° C.	400° C.	500° C.	600° C.	700° C.	800° C.	950° C.
CO + S, % .				0·5	1·5	6	16	33	64
$CO_2 + CS_2$, %	19	27	34	39	42	43	41	33	19
COS, % . .	81	73	66	61	56	51	43	34	17

The above investigators found that the $COS \rightleftarrows CO + S$ reaction is catalysed by platinum, though the metal is poisoned. The $2COS \rightleftarrows CO_2 + CS_2$ reaction is catalysed by quartz or glass and is independent

* Paper received December 12th, 1935.

from pressure. The reaction $2COS \longrightarrow CO_2 + CS_2$ is very slow compared with the reaction $CO + S \longrightarrow COS$. In fact, when treating organic sulphur with CO at 300° C. and 1000 lb. per sq. inch pressure in presence of MoS_3 on silica gel or kaolin, CS_2 was not found in the gas mixture. For that reason the $2COS \longrightarrow CO_2 + CS_2$ reaction was neglected and the investigation based on the $CO + S \rightleftarrows COS$ equilibrium which is as follows:

TABLE II.

Temperature	400° C.	500° C.	600° C.	700° C.	800° C.	950° C.
CO + S, %	0·5	2·5	9	24	47	77
COS, %	99·5	97·5	91	76	53	23

From Table II it can be seen that complete removal of sulphur from the gas mixture would be at temperatures below 400° C. A treating temperature of 300° C. was considered as the most suitable and selected in this investigation. With the increase of this temperature, undesirable cracking would take place when treating mineral oils. With the decrease of this temperature the reaction rate would decrease.

The reacted gas contained considerable amounts of CO_2. This was due to decomposition of CO according to the reaction:

$$2CO \rightleftarrows CO_2 + C$$

and also to the presence of water when a wet catalyst, which was found to be more active, was used. Then the reactions:

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$
$$CO + H_2O \rightleftarrows CO_2 + H_2$$

took place.

The first of these reactions will be on the CO_2 side at high pressure. At atmospheric pressure the equilibrium of this reaction is as follows:

TABLE III.

Temperature	450° C.	500° C.	600° C.	700° C.	800° C.	900° C.	1000° C.
CO_2, %	98	95	77	42	7	3·5	0·5
CO, %	2	5	23	58	93	96·5	99·5

Without catalyst the decomposition of CO into carbon at red heat is very slow. In the presence of highly active catalysts this reaction takes place at a temperature near 300° C.

Another reaction which may take place, and would consume an excess of CO, is the reduction of the sulphide catalyst:

$$MoS_3 + CO = MoS_2 + COS.$$

EXPERIMENTAL.

As a preliminary survey of catalysts gave the best results with MoS_3, a series of experiments shown in Table IV was undertaken with this catalyst in an attempt to establish the working conditions.

TABLE IV.

Showing the Effect of Catalysts on Desulphurization with CO.

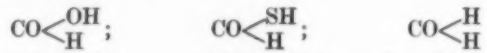
Expt. No.	Product treated.	Catalyst.	Temperature of treatment, ° C.	Pressure : Initial (lb.).	Pressure : Final (lb.).	Duration of experiment (hours).	% Sulphur in the initial product.	% Sulphur in liquid after reaction.	Total Sulphur in the gas after treatment (mg./litres).	Remarks.
1	Thiophene in toluene	MoS_2	315	1000	400	6	0·85	0·08	44	
3	Pressure distillate boiling 135–206° C.	MoS_2	315	1000	400	6	0·73	0·22	44	
5	Thiophene in toluene	Pd on asbestos	320	900	890	3½	0·78	0·67	3	
6	Thiophene in toluene	MoS_2	325	1000	440	4	0·78	0·04	—	
8	Thiophene in toluene	CoS	300	950	700	4½	0·81	0·42	—	
9	Heptyl sulphide in toluene	MoS_2	320	1000	640	4	0·67	0·03	103	Spent Catalyst Mo, 54·8 Ratio S, 36·7 Same as MoS_2
28	Thiophene in toluene	MoS_2	310	1000	570	2½	0·84	0·38	—	CO_2 19·2% COS 2·7% CO 70·0% CO_2 0·0% O_2 0·7% Co 96·1% Composition of reacted gas
30	Toluene blank	No	310	910	930	6	0·0	0·0	—	
31	Thiophene in toluene	Catalyst 28	295	1000	400	4	0·84	0·32	—	
33	Thiophene in toluene	MoS_2, very dry	300	1000	700	5	0·84	0·73	—	

The MoS_3 catalyst was prepared according to Tropsch [2] by decomposing a solution of ammonium sulphomolybdate, $(NH_4)_2MoS_4$, with dilute sulphuric acid, washing the precipitated MoS_3 and drying it in a vacuum at 60° C. Some catalysts were heated at higher temperature than according to Tropsch.

Each experiment was made with 50 ml. of liquid. The treated liquids were solutions of thiophene in toluene, a solution of heptylsulphide in toluene and two pressure distillates. The pressure distillate shown in experiment 3 contained 0·73 per cent. sulphur, had a specific gravity $D_4^{20} = 0{\cdot}798$, boiling range 135–206° C., and was a product treated with 6 lb. sulphuric acid per barrel. The pressure distillate shown in experiment 45 contained 0·94 per cent. sulphur, had a boiling range 175–200° C., and was a product treated with 2 lb. sulphuric acid. It was supposed to contain, mainly, the most stable tetramethylthiophene. The amount of catalyst used, in all cases, was about 5 gm. The carbon monoxide was about 99·0 per cent. pure and analysed about 1 per cent. air. The initial pressure of CO was from 900 to 1000 lb. per sq. inch in all experiments. The sulphur in the reacted gas was determined by the A.S.T.M. lamp method. The sulphur was present as COS and H_2S. The H_2S was perhaps formed by hydrolysis of COS when water was present. The COS value was determined by absorption in a weak sodium hydroxide solution. All experiments were made at 300° C. as close as possible. The duration of the experiment does not include the heating time from room temperature to 300° C., which was about 1 hour. Each experiment was made with MoS_3 freshly prepared if not otherwise stated.

It appeared that the reduction of sulphur was not so good on catalysts dried to completion in a high vacuum, or when using a higher drying temperature than 60° C., such as 110° C. This was the case in experiments 28, 31 and 33, shown in Table IV, and in a number of other experiments not recorded here due to similarity of results. The moisture could have a protective effect on the pyrophoric MoS_3. It is known that MoS_3 treated with CO_2 loses its pyrophoric character without losing its hydrogenation activity.

The more probable explanation is that traces of water make the CO active. Carbon monoxide, although an unsaturated compound, is inactive like nitrogen, with which it shares a common molecular weight of 28, which explains its inactivity from the theoretical standpoint. From the work of Wieland,[3] on oxidation of CO, it is known that carbon monoxide is activated by gaseous hydrides, *e.g.* H_2O, H_2S, NH_3, C_2H_4, etc., while hydrogen-free gases like SO_2, CO_2, N_2O, etc., have no effect. The action is possibly due to compounds such as



Formic acid. Thioformic acid. Formaldehyde.

Although these compounds are not formed by direct union, the affinity exists, which might be the cause of activation. In case of water in presence of catalysts, a part of the CO is converted into CO_2 according to the reaction:

$$CO + H_2O = CO_2 + H_2.$$

TABLE V.

Showing the Effect of H_2O *and* H_2S *on the Efficiency of* MoS_2.

Expt. No.	Product treated.	Catalyst.	Temperature of treatment (° C.).	Pressure: Initial (lb.).	Pressure: Final (lb.).	Duration of experiment (hours).	% Sulphur in the initial product.	% Sulphur in the liquid after reaction.	Remarks.
37	Thiophene in toluene	MoS_2 slightly moist	300	1000	540	5	0·84	0·06	
38	Thiophene in toluene	MoS_2 dried completely with H_2S at atmospheric pressure at 110° C.	300	1000	500	5	0·84	0·12	CO_2 = 49·4%; COS = 6·0%; Total S = 136 mg./L.
40	Thiophene in toluene	MoS_2 dried in vacuum with H_2S at room temperature	300	1000	700	4	0·84	0·65	CO_2 = 6·5%; COS = 2·1%; Total S = 41 mg./L.
42	Thiophene in toluene	Sample 40, 5 drops of water	300	1000	500	6	0·81	0·42	CO_2 = 21·6%; COS = 4·1%; Total S = 70 mg./L.
43	Thiophene in toluene	MoS_2 dried at 80° C. with H_2S in vacuum	300	1000	500	6	0·81	0·06	
44	Thiophene in toluene	MoS_2 very dry	305	950 CO, 50 H_2S	500	5½	0·85	0·14	
45	Pressure distillate boiling 175–200° C.	Sample 43	305	1000	510	4½	0·95	0·27	

Having this explanation as a leading factor, another series of experiments, shown in Table V, was made. Experiment 37 made with a slightly moist MoS_3 showed a reduction of sulphur from 0·84 per cent. to 0·06 per cent. The experiments 38, 42, 44, where H_2S was applied, showed good reduction of sulphur with exception of experiment 40, in which the catalyst had insufficient H_2S due to application of high vacuum during the drying. When five drops of water were added to the catalyst 40 the reduction of sulphur was increased as shown in experiment 42. The pressure distillate in experiment 45 was a very sulphur stable product and showed a reduction from 0·95 per cent. to 0·27 per cent.

Two experiments were made in a vapour phase at atmospheric pressure in a heated vertical, 1 inch diameter, iron pipe charged with 15 gm. MoS_2 deposited on 150 gm. pumice stone of 15 mesh. A solution of thiophene in toluene, containing 0·60 per cent. sulphur, was passed through the catalyst at 300° C. at a rate of 1 ml. per minute. The carbon monoxide gas passed in the same direction with the hydrocarbon vapours at a rate of 150 ml. per minute. The treated liquid analysed 0·55 per cent. sulphur. The amount of solution injected was 75 ml. This experiment was continued by injecting 30 ml. of the toluene solution with a rate of 0·05 ml. per minute. The treated liquid analysed 0·32 per cent. sulphur.

Conclusions.

It has been shown on a solution of thiophene in toluene, which analysed in average 0·85 per cent. sulphur, that sulphur can be eliminated, leaving about 0·05 per cent. when treating for 4 hours with CO under an initial gas pressure of 1000 lb. in a closed autoclave at 300° C. with MoS_3 as catalyst. Other catalysts are active, but their efficiency is not known. Under same conditions of experiment a pressure distillate with a boiling range of 175–200° C., which mainly contained the most stable tetramethylthiophene, was reduced in sulphur from 0·95 per cent. to 0·27 per cent. The dried MoS_3 catalyst is not always equally effective. It appears that small amounts of moisture or H_2S are required to activate the carbon monoxide. This point has to be proven by further experiments.

A vapour-phase treatment of a solution of thiophene in toluene, with CO at atmospheric pressure at 300° C. over MoS_3, showed a reduction of sulphur from 0·60 per cent. to 0·32 per cent.

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[2] H. Tropsch, *Brenn.-Chem.*, 1930, **11**, 450.
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THE CONVERSION OF PETROLEUM GASES INTO USEFUL HYDROCARBON PRODUCTS.

Presented on behalf of the Staff of the Anglo-Iranian Oil Co.'s Research Station at Sunbury, Middlesex.

By A. E. DUNSTAN, D.Sc., F.I.C., F.C.S (Past-President), and D. A. HOWES, Ph.D. (Associate Member).

INTRODUCTION.

CONSIDERABLE attention has been devoted, during the past twenty years, to the profitable utilization of petroleum gases. Numerous processes have been worked out whereby these gases may be converted into valuable organic chemicals and chemical intermediates, but in cases where the amount of gas to be handled is very large, such outlets are not promising, and this paper is concerned entirely with the production of synthetic hydrocarbons boiling in the gasoline range.

Intensive research and development work in the field of petroleum gas utilization have been carried out during the past ten years with two objects in view. At the outset, the object was almost entirely one of conservation. The gases available were waste products, and it was desired to convert these into marketable material. The quantities of gas concerned were too enormous to allow consideration of special chemical production and attention was concentrated on the production of synthetic hydrocarbon spirits. Then a further demand arose which was no less urgent. This demand was for the highest-quality motor fuel, and research carried out on gas utilization showed the two requirements of conservation and super-quality products could be met simultaneously.

WASTE GASES AVAILABLE.

Two main types of waste gases have received attention :—(*a*) Straight-run paraffinic gases, (*b*) cracked gases.

The first are obtained in association with crude oil at the well-head, and

TABLE I.

	CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	C_2H_4.	C_3H_6.	C_4H_8.
	Per cent. by volume.						
1. Straight-Run Gas.							
(*a*) Lean . .	78	20	1	1	—	—	—
(*b*) „ . .	46	27	18	9	—	—	—
(*c*) Rich . .	—	—	25	75	—	—	—
2. Cracked Gas.							
(*a*) Lean . .	46	17	9	4	14	7	3
(*b*) Rich . .	—	9	27	18	7	24	15
(*c*) „ (Stabilizer overhead) .	6	20	26	13	4	16	15

a further quantity is obtained on crude oil distillation. The second are obtained in cracking operations of various kinds. The composition of each type of gas varies according to conditions of production, fractionation, etc., but the compositions given in Table I are indicative.

For special purposes these gases may be compressed and fractionated, or the different hydrocarbons separated by any of the various means now available. Some of the gases contain hydrogen sulphide, but this may, in some cases, be removed by fractionation, or, where fractionation is not possible, desulphurization may be effected by obvious chemical processes.

Classification of Methods of Gas Utilization.

The methods available for the production of higher molecular weight hydrocarbons (*e.g.* motor spirit) from petroleum gases may be classified as follows.

A. *Applicable to both Saturated and Unsaturated Gases.*

1. High-temperature, low-pressure pyrolysis primarily to produce aromatic hydrocarbons—the so-called Benzole Pyrolysis.
2. Low-temperature, high-pressure treatment involving pyrolysis and subsequent polymerization in the case of saturated gases and only polymerization and condensation in the case of unsaturated gases.

B. *Applicable to Saturated Gases.*

1. Pyrolysis to unsaturated hydrocarbons followed by polymerization processes.
2. Dehydrogenation to unsaturated hydrocarbons followed by polymerization processes.

C. *Applicable to Unsaturated Gases.*

1. Catalytic Polymerization.
2. Sulphuric Acid Polymerization.

In addition, there are various processes by which saturated and unsaturated hydrocarbons may be condensed—so-called Alkylation Processes.

The gasolines produced by some of the above processes may be improved by non-destructive hydrogenation—*i.e.*, reduction of olefinic products to the corresponding saturated hydrocarbons.

In this classification the term high-pressure is applied to pressures above 300 lb. gauge and the term high-temperature to temperatures above 600° C.

Properties of Petroleum Gases, and Yields of Liquid Products Obtainable.

The gaseous paraffins and olefines, from methane to butane, vary in specific gravity (air = 1) from 0·55 to 2·0, consequently the maximum yield of synthetic gasolines obtainable therefrom, expressed in Imperial gallons per 1000 standard cubic feet, varies between fairly wide limits.

For any gaseous hydrocarbon, assuming the perfect gas laws to be obeyed, 1 mole occupies 22·4 litres at N.T.P. or 23·7 litres at 60° F. and 760 mm. These figures are equivalent to 358·8 cubic feet per lb. mole at N.T.P. or 379·3 cubic feet per lb. mole at 60° F. and 760 mm.

TABLE II.

	Grams per litre at 60° F. and 760 mm.	Lb. per cubic foot at 60° F. and 760 mm.
Methane . . .	0·678	0·0421
Ethane . . .	1·263	0·0791
Propane . . .	1·860	0·116
Butanes . . .	2·45	0·153
Ethylene . . .	1·18	0·074
Propylene . . .	1·77	0·111
Butylenes . . .	2·37	0·148

The densities of the hydrocarbon gases are as given in Table II, assuming the ideal gas laws to be obeyed.

The maximum obtainable yield of liquid product from these gases by

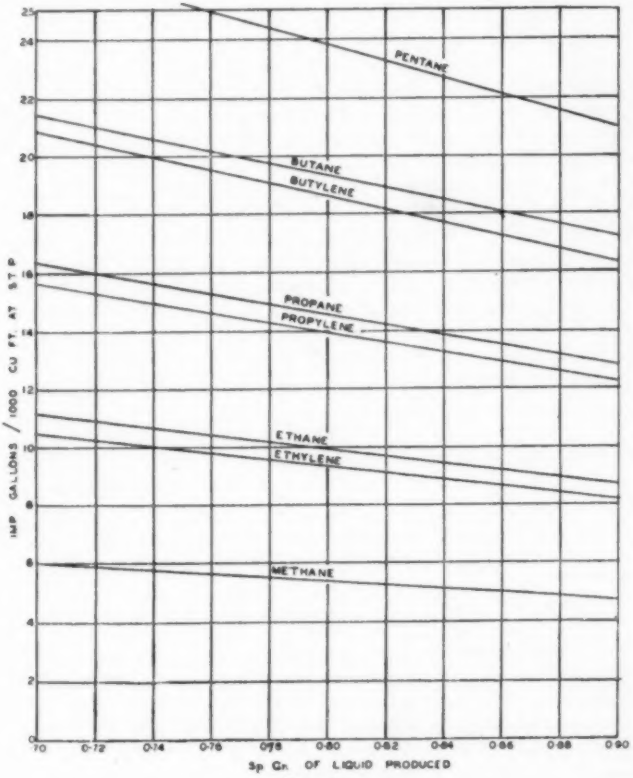


FIG. 1.

THEORETICAL YIELDS (100% CONVERSION) OF LIQUIDS OF SP. GR. 0·7 TO 0·9 OBTAINABLE FROM GASEOUS HYDROCARBONS.

processes of pyrolysis or polymerization which do not involve reaction with any extraneous substance is therefore given by the relationship:

$$\text{Gallons per 1000 cu. ft.} = \frac{\text{lb. per cubic foot} \times 1000}{\text{sp. gr. of liquid produced} \times 10}$$

Fig. 1 gives in convenient form the yield of liquid product obtainable from the gaseous hydrocarbons at 100 per cent. weight conversion in terms of Imperial gallons per 1000 cu. ft. for product specific gravities ranging from 0·700 to 0·900. It is evident that higher liquid yields are theoretically obtainable from a given volume of butane than from the same volume of, say, methane. From the point of view of plant size, therefore, the most economical operation is obtained on rich gas feed stocks.

A. Methods Applicable to both Straight-run and Cracked Gases.

(1) *High-Temperature, Low-Pressure Pyrolysis for Benzole Production.*

This process has been completely developed in these laboratories, and all difficulties attending the very high temperatures employed have been satisfactorily overcome. To obtain a product rich in benzene the temperature conditions must necessarily be severe, but the yields obtainable are sufficiently high to attract attention. The temperature required at substantially atmospheric pressure operation varies from 1000 to 1200° C. (1832–2192° F.) in the case of methane to 800–850° C. (1472–1562° F.) in the case of butane, and under these conditions the representative yields of total liquid, 200° C. end-point benzole and residue boiling above 200° C. obtained are as shown in Table III. By operating under temperature and pressure conditions less severe than those required for the production of benzole, the liquids obtained are essentially unsaturated in character and are of lower octane number than benzoles. Under reaction conditions suitable for benzole production, by making small variations in temperature, throughput or pressure, it is possible to alter the freezing point, boiling

Table III.

Yields of Products Obtainable by the Benzole Pyrolysis of Pure Hydrocarbons.

Atmospheric pressure operation. Constant reaction time.

Hydrocarbon.	Temp. (° C.).	Total liquids.		200° E.P. Benzole.		Residue above 200° C.	
		Gal./ 1000 cu. ft.	Per cent. weight.	Gal./ 1000 cu. ft.	Per cent. weight.	Gal./ 1000 cu. ft.	Per cent. weight.
Paraffins:							
Methane	1050	0·44	8·8	0·3	4·7	0·14	4·1
Ethane	900	2·1	21·9	1·5	16·9	0·6	5·0
Propane	850	3·25	23·09	2·4	18·4	0·85	4·69
Butanes	850	4·6	24·55	3·4	19·8	1·2	4·75
Olefines:							
Ethylene	800	3·15	36·1	2·4	28·8	0·75	7·3
Propylene	800	5·32	40·6	4·0	31·2	1·32	9·4
Butylenes	800	6·85	39·6	5·1	30·7	1·75	8·9

range and unsaturated content of the product at will, and under the most severe conditions employed, a 200° E.P. distillate consisting largely of benzene (C_6H_6, b.pt. 80·8° C.) can be obtained.

In the benzole pyrolysis process the variables temperature, pressure and throughput rate are to a large extent complementary, although there is a minimum temperature below which benzole formation is not obtained. If super-atmospheric pressure is employed as a means of increasing plant throughput, the temperature remaining the same as in atmospheric pressure operation, then the same type of product will be obtained, but if, by the use of pressure, a lower reaction temperature is used, then the product will only be substantially benzene if the temperature is above about 800° C. At lower temperature products containing toluene, xylene and higher aromatics are obtained. Data are given in Table IV showing how variation of reaction conditions affects the properties of the 200° E.P. distillates obtained.

The results of tests made on the treatment of propane, butane and natural gas fractions at 525–575° C. (977–1067° F.) and at pressures of 250–1000 lb./sq. in. have been recently described by Tropsch, Thomas and Egloff,[1] but the liquid products so obtained were of lower gravity and octane number than those under discussion. They cannot be described as entirely aromatic. On the other hand, Cooke, Swanson and Wagner[2] have described tests on cracked gas feeds at 1150–1300° F. (621–704° C.) and 65 lb./sq. in. which yield distillates very similar to the less aromatic of those described in Table IV. When cracked gases are processed, the temperatures required for benzole production are lower than in the case of the corresponding paraffins.

Exhaustive tests in these laboratories have shown that the benzoles obtained by the pyrolysis of gaseous hydrocarbons may be easily refined to yield good colour spirits of very satisfactory gum stability in conventional refining plant. Sulphuric acid may be used as the refining agent. The amount required is only in the order of 0·3 per cent., a quantity not greater than that required in the refining of cracked spirits. The refined spirits have been subjected to prolonged engine tests in which gum formation has been encouraged, but the amount of gum deposition in the inlet manifold and on the inlet valves is negligible.

The product may thus be described as a fully satisfactory benzole of natural gas origin.

With regard to the knock ratings and blending properties of benzoles produced by pyrolysis, these are very similar to those of pure benzene and are referred to in detail later.

Plant for Pyrolysis Reactions.

The plant required for the production of benzole by the pyrolysis of gaseous hydrocarbons is very simple, and only consists of conventional refinery equipment, although the choice of materials and reaction conditions is important. A typical flow diagram is reproduced in Fig. 2.

It is usually convenient to avoid the use of feed stocks in the gaseous state and to liquefy in normal stabilizing equipment. This allows the use of inlet feed pumps and the avoidance of compressors with their attendant high running and maintenance costs. Modern stabilizing equipment

TABLE IV.

Properties of Pyrolysis Benzoles—Affect of Variation in Reaction Conditions.

Inlet gas. Straight-run gas. $C_2H_6 = 15\%$, $C_3H_8 = 20\%$, $C_4H_{10} = 45\%$, $C_5H_{12} = 20\%$.

Temperature (° C.)	700	750	800	850	870	800	850	850
Inlet Pressure (lb./sq. in.)	30	30	30	30	5	5	5	15
Space velocity (vol. inlet gas/vol. reaction space/hr.)	209	209	209	209	210	182	182	400
Properties of Product :—								
Sp. gr. at 60° F.	0·796	0·849	0·873	0·875	0·880	0·845	0·873	0·875
Initial b. pt. (° C.)	39	51	69	70	69	66·5	67·5	63
10 per cent. distillate at	55	70·5	79	80	80	80	78·5	76·5
20 ,, ,,	62	77	81	82	82·5	84	81	79·5
30 ,, ,,	68·5	81	82·5	83	84	87·5	82	81
40 ,, ,,	75	84	84	84	86	91	83·5	83
50 ,, ,,	81	87	85	85	87·5	96·5	85	84
60 ,, ,,	87	90	87	86·5	89·5	107	86	86
70 ,, ,,	94·5	94·5	89·5	89	94	133·5	88·5	88·5
80 ,, ,,	109	102·5	95	93·5	102	169	93	93
90 ,, ,,	153	125	113	110	130	188·5	109·5	109
Final b. pt. ,,	211	190	187	200	200	200	200	195
Aniline point (° C.)	<0° C.	<0° C.	<0° C.	<0° C.	<0° C.	<0° C.	<0° C.	<0° C.
Bromine number (grm./100 g.)	74	56	25	22	—	—	—	—
Octane number (C.F.R. Motor)	84·4	95·6	96·1	104·1	102	87·7	101·5	30
Freezing point (Air Ministry test) (° C.)	−38° C.	−19	−17	−7	—	—	—	99
Blending Octane Number :—								−15° C.
20 per cent. in 52·5 octane number base	104·8	—	—	—	100·2	—	—	—
30 ,, 65 ,, ,,	91·6	93	—	—	92	—	—	—
30 ,, 70 ,, ,,	87·3	90·3	—	—	88·6	—	—	—

operates at pressures up to 500 lb./sq. in., and there is usually no difficulty in obtaining feed stocks in the liquid state, except in the case of those containing large amounts of non-condensable gases such as ethylene. In such cases compressors must be used. The plant required comprises a preheat furnace, reaction coil (either heated or unheated), cooling device, tar separator, product receiver and product stabilizer.

Furnaces.—The preheat furnace may be conventional pipe-still practice, although the selection of the furnace tubes and furnace insulation for use at temperatures above 500° C. (932° F.) and up to 880–900° C. (1616–1652° F.) needs care. Up to temperatures of 500° C. ordinary cracking furnace tubes may be employed, fabricated in mild steel, 0·5 per cent. molybdenum steel or 6 per cent. chromium steel, but, for the higher temperatures, steel containing higher percentages of nickel and chromium are required. Stainless steels of the 18/8 chromium–nickel type are satisfactory for tempera-

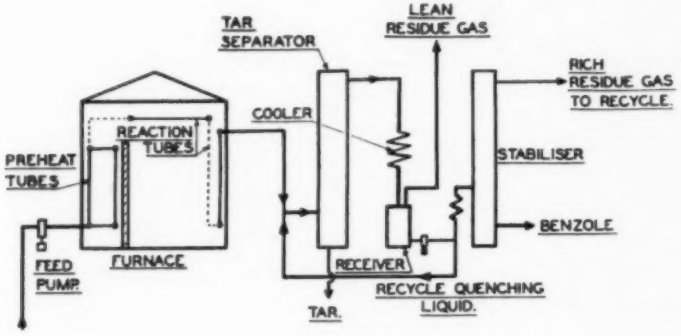


FIG. 2.

FLOW DIAGRAM. PYROLYSIS OF GASEOUS HYDROCARBONS FOR BENZOLE PRODUCTION.

tures not exceeding 650° C., but reasonable tube life at temperatures up to 900° C. (1652° F.) is only obtained by the use of 25/20 chromium–nickel steels, examples of which are Hadfields H.R.3 and Krupps N.C.T.3. Tests carried out on a semi-commercial plant over several years have demonstrated that such steels are perfectly satisfactory for continued service because of their excellent mechanical properties and resistance to decarburization and scaling.

The reaction coil is preferably heated in pyrolysis processes as markedly endothermic as that involving benzole production, and is normally placed in the same furnace as the preheating tubes. The reaction coil may, however, be unheated when handling olefinic feed stocks and mounted on an independent structure; in this case it is desirable to provide means for fairly rapid cooling, such as controlled induced or forced-air circulation. In the production of benzole from saturated gases such as propane or butane the heat absorbed by reaction is approximately 1000 B.Th.U. per lb. of inlet gas, excluding the heat required in preheating the feed to reaction temperature. This figure is materially lower in the case of feed stocks

containing unsaturateds because the latter undergo exothermic reactions during the initial stages of the pyrolysis process. To avoid sagging of furnace tubes, these may be mounted vertically and supported only from the top.

The formation of coke and carbon in the furnace tubes may be reduced to that normally met with in cracking plant practice by careful attention to the flow conditions of the gases being treated. Highly turbulent flow and short heating periods are necessary. Values of $\frac{vD}{\nu}$, where v = gas velocity cms./second, d = diameter of tube cms., ν = kinematic viscosity stokes, should be at least 10,000–20,000 for efficient heat transfer and to avoid coke deposition. Recycle operation is also favourable with regard to prevention of coke formation.

Various patents cover the use of linings for pyrolysis furnace tubes which inhibit carbon formation. Such linings are effective for short periods, but eventually become coated with a thin layer of carbon and coke, and so lose their efficacy. Similarly, any differences which exist between different furnace-tube materials with regard to catalytic or auto-catalytic effect on carbon deposition disappear after a comparatively short period when the inside of the tube acquires a thin coating of carbon.

Proposals have been made from time to time to employ as furnace tube materials for pyrolysis processes, cheap steels, such as mild steel treated in various ways to give an outside surface of heat-resisting alloy. Such composite materials rarely possess adequate mechanical strength, and often give trouble due to excessive creep.

Coolers and Tar Separators. The exit gases from the preheat and reaction furnaces must be cooled to a temperature suitable for tar removal and stabilization. This is conveniently accomplished by injection of cold oil, by heat exchange with the inlet feed to the furnaces or by a combination of atmospheric coolers and conventional water coolers. Tar separation may be effected by flashing into a separator under suitable temperature and pressure conditions or by the use of electrostatic detarrers at temperatures about 100° C.

Product stabilizers follow normal refinery practice.

Composition of Residue Gases from Benzole Pyrolysis Processes.

By the treatment of C_3 and C_4 hydrocarbons at pressures of 5–100 lb./sq. in. and temperatures of 750–900° C. at suitable throughput rates, single pass treatment is sufficient and recycling can be avoided. Under these conditions the exit gas from the product stabilizers has the following average composition :—

Hydrogen	10–25% volume.
Methane	50–65% ,,
Ethylene	20–25% ,,
Ethane	0–10% ,,

This gas is a refractory pyrolysis stock, but the ethane–ethylene fraction may be treated in this way after separation, or it may be subjected to polymerization. The hydrogen–methane fraction constitutes an ideal feed for hydrogen manufacture by well-known processes.

Properties of Tars Produced (i.e. *Liquids Boiling above* 200° C.).

The tars produced in the benzole pyrolysis reaction consist almost entirely of polynuclear aromatic hydrocarbons, naphthalene and anthracene predominating, and are solid crystalline masses at ordinary temperatures. They constitute valuable sources of the higher aromatic hydrocarbons, and by destructive hydrogenation may be converted, with good yield, into gasolines of 90–100 octane number having very low freezing points and good blending properties.

(2) *High-Pressure, Low-Temperature Polymerization Processes.*

As an alternative to the pyrolysis of gaseous hydrocarbons at temperatures above 700° C. and at pressures up to about 300 lb./sq. in. there are also available various other methods by which good yields of synthetic gasolines may be obtained and which involve the use of pressures of 500–4000 lb./sq. in. at temperatures up to 600° C. In these processes polymerization is the most important reaction, as distinct from pyrogenic decomposition, although some of the paraffins are decomposed to olefines prior to polymerization or otherwise take part in the reaction if the conditions of temperature, pressure and reaction time are favourable.

The olefines, ethylene, propylene and butylene, easily undergo polymerization reactions in the absence of catalysts at temperatures as low as 350° C. at 500 lb. pressure. Increase of pressure is favourable to the reaction, which causes a decrease in volume of the reactants, whilst increase in temperature has a very pronounced effect in increasing the speed of the reaction. This process has been very thoroughly examined on both the laboratory and semi-commercial scales during the past few years, and complete success has been obtained. Unfortunately, the octane numbers of the synthetic gasolines are not as high as those of pyrolysis benzoles, although the yields are higher.

In a previous paper [3] attention was directed to the fact that ethylene, when heated under polymerization conditions of temperature and pressure, is liable to spontaneous and explosive decomposition to carbon, hydrogen and methane. This occurrence has not been observed on either propylene or butylene, or when working with gaseous mixtures containing up to 25 per cent. by volume of ethylene at temperatures up to 500° C. and pressures up to 2500 lb./sq. inch. The phenomenon does not occur with normal refinery gases.

A flow diagram of the semi-scale plant employed in the investigation of the non-catalytic polymerization process is reproduced in Fig. 3. The feed stocks examined were vapour-phase cracked gas and stabilizer overhead, of the compositions given in Table I. These were fed to the plant by compressor and pump respectively, and passed through a preheat coil and reactor in series, and thence to a cooler, H.P. separator and product stabilizer. The plant designed was capable of operation at temperatures up to 650° C. and at pressures up to 4500 lb./sq. in., so that the reaction variables could be studied over a wide range.

As in the case of pyrolysis to benzole, it was found that desulphurization of the feed stock was desirable in order to avoid corrosion and the fixation of the sulphur in the product in the form of mercaptans and sulphides, with resultant increased refinery difficulties.

The polymerization reaction is markedly exothermic, and it was not found necessary to heat the reactor. In fact, when operating at high con-

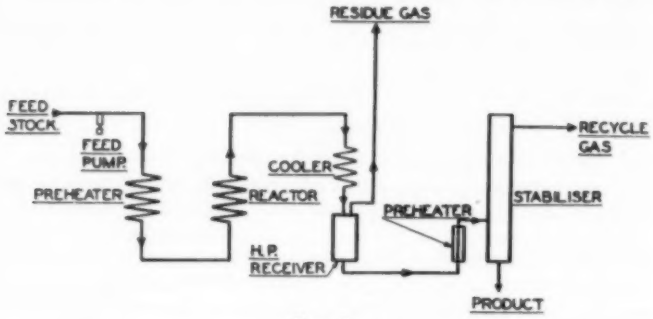


FIG. 3.

FLOW DIAGRAM. SEMI-COMMERCIAL THERMAL POLYMERIZATION PLANT.

versions per pass, considerable difficulty was experienced in preventing the reactor temperatures getting out of control, and means for sudden

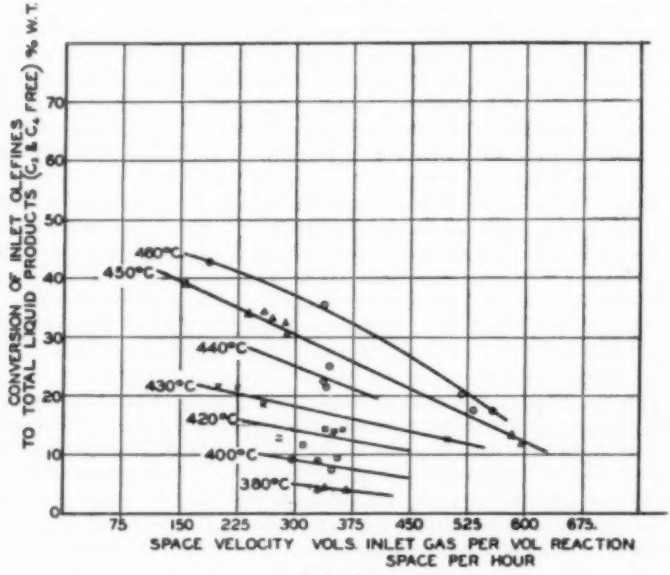


FIG. 4.

THERMAL POLYMERIZATION OF STABILIZER OVERHEAD. EFFECT OF INLET GAS RATE AND TEMPERATURE ON CONVERSION AT 800 LB. PRESSURE.

chilling were adopted. Careful temperature control was found necessary to avoid the formation of coke. Another factor controlling the amount of

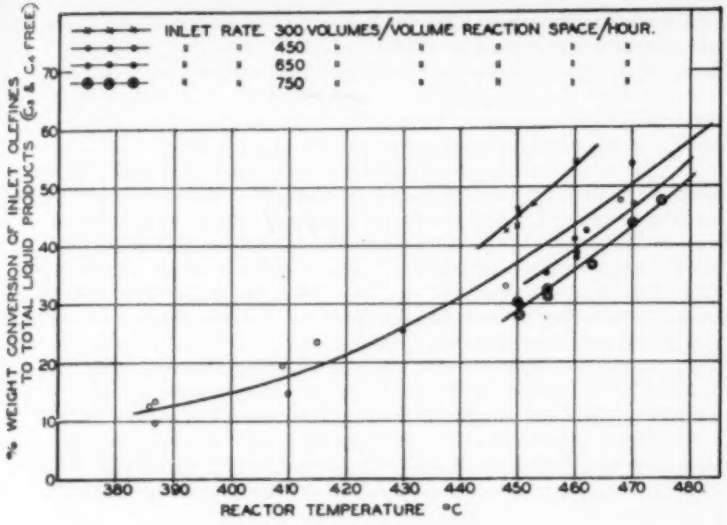

INLET RATE 300 VOLUMES/VOLUME REACTION SPACE/HOUR.
450
650
750
% WEIGHT CONVERSION OF INLET OLEFINES TO TOTAL LIQUID PRODUCTS (C3 & C4 FREE)
REACTOR TEMPERATURE °C

FIG. 5.

THERMAL POLYMERIZATION OF STABILIZER OVERHEAD. RESULTS OBTAINED AT 1300 LB. PRESSURE.

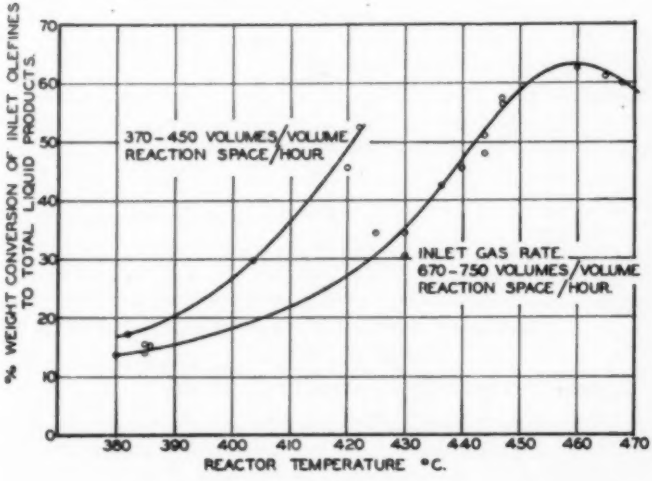

370-450 VOLUMES/VOLUME REACTION SPACE/HOUR
INLET GAS RATE 670-750 VOLUMES/VOLUME REACTION SPACE/HOUR.
% WEIGHT CONVERSION OF INLET OLEFINES TO TOTAL LIQUID PRODUCTS.
REACTOR TEMPERATURE °C.

FIG. 6.

THERMAL POLYMERIZATION AT STABILIZER OVERHEAD. RESULTS OBTAINED AT 2000 LB. PRESSURE.

coke deposition was the time of reaction. When this was prolonged to get high conversions per pass, coke formation readily occurred, but by limiting the conversion per pass to 60–70 per cent. this was prevented. This necessitates the use of a recycle system if the optimum yields are required.

A selection of typical results obtained are given in Figs. 4–6. These show the effect of pressure, temperature and reaction time on conversion, and refer to a stabilizer overhead feed stock, as mentioned in Table I.

The process is an easy one to operate. The reaction conditions are not unduly critical, and are determined by the nature of the product required and the capital and running costs of the plant. Under optimum conditions, the product contains about 80 per cent. by weight of 200° C. end-point distillate, the remainder being a residue of little value as a high-speed diesel fuel, but a satisfactory stock for cracking or destructive hydrogenation. Unfortunately the gasoline produced under the most favourable conditions is little superior to normal cracked spirit in octane number, and has an optimum value of 75–80 (C.F.R. Motor Method) when produced at 480–550° C. and 500–1000 lb. pressure. In addition the lead responses are poor. At lower temperatures the gasoline octane numbers are lower.

The most important effect of pressure in the thermal polymerization process is to increase the throughput capacity of a given size plant, but another valuable effect is a reduction in the temperature necessary to effect a given conversion per pass.

Typical properties of thermal polymers produced from stabilizer overhead of the composition given in Table I, at 1000 lb. pressure and 510° C. are set out in Table V.

TABLE V.

	Crude Polymer.	Crude 200° C. E.P. distillate.	Residue Above 200° C.
Sp. gr. 60° F.	0·780	0·764	0·985
Initial b. pt. (° C.)	23° C.	27	222
2% distillate at	—	35	—
5% " "	—	46	—
10% " "	60	58	236
20% " "	82	77	250
30% " "	95	91	266
40% " "	100	99	280
50% " "	110	103	297
60% " "	130	114	317
70% " "	150	123	335
80% " "	180	145	—
90% " "	230	178	—
Final b. pt.	320	198	—
% 100° C.	40	41	—
% 140° C.	64	77	—
% 200° C.	84	—	—
% 300° C.	—	—	52
Total distillate	97	98	75
Residue	1	1	25
Loss	2	1	—
Aniline Point (° C.)	—	272	Below 15° C.
Bromine number	—	75	20
Freezing Point (° C.)	—	Below −70	—
Gum Actual	—	35 mg./100 ml.	—
Reid Vapour Pressure	—	4·5 lb. at 100° C.	—
Octane number (C.F.R. Motor)	—	75	—
" " C.F.R. Research	—	89	Cetene No. 19

The gasoline fractions of thermal polymers produced from cracked feed stocks such as stabilizer overhead fractions, containing both propylene and butylene, show no improvement in octane number on non-destructive hydrogenation. However the polymer gasolines may readily be refined to marketable products of most satisfactory quality.

B. Methods Applicable to Saturated Gases.

(1) *Pyrolysis to Unsaturateds followed by Polymerization Processes.*

The saturated gases, ethane, propane and butanes, may readily be cracked to olefines by exposure at temperatures from 650° C. to 1100° C. for short time intervals, the reaction time required being reduced by an increase of temperature within this range.

This gas cracking process has been investigated in considerable detail both in laboratory and semi-commercial scale equipment, as a means of producing anti-knock material from natural and straight-run refinery gases —the olefines produced being subsequently polymerized by thermal or catalytic processes. The reaction conditions preferred for the production of olefines from propane–butane mixtures are 750–900° C., low pressure, *e.g.* up to 30 lb. gauge and inlet gas rates of 200–2500 volumes per volume of reaction space per hour (measured at S.T.P.). Under these conditions coke formation is negligible and no oils or tars are produced. The reaction is endothermic, and the reaction coil must be heated. Highly turbulent flow is important if good heat transfer is to be obtained and if coke deposition is to be avoided.

The optimum results obtainable from a 2/1 mixture of propane–butane may be summarized as follows :—

Volume conversion to olefines = 100–120 per cent.
Weight conversion to olefines = 50–60 ,,
Olefines produced—lb./cu. ft. reaction space/hour = 200–1000.

The olefines produced consist mainly of ethylene—the higher olefines suffering degradation in the reaction. This is a disadvantage, and for high yields of propylene and butylene resource must be made to catalytic dehydrogenation.

(2) *Dehydrogenation of Saturated Gases.*

In contradistinction to the pyrolysis of saturated hydrocarbons such as propane or butane, in which the scission of carbon chains takes place, it is theoretically possible to produce olefines from the corresponding paraffins by the simple removal of hydrogen—*i.e.* " dehydrogenation."

$$\textit{e.g.}\ C_4H_{10} \longrightarrow C_4H_8 + H_2$$
Butane —— Butylene + Hydrogen.

The fundamental difference between pyrolysis and dehydrogenation as a means of producing olefines is that in the latter process, hydrocarbons containing a lower number of carbon atoms to the molecule than the original paraffin are not produced, *i.e.* no cracking takes place, whereas in pyrolysis cracking is the main reaction.

Of particular importance is the production of butenes from straight-run

butane—which may be polymerized to dibutenes and then hydrogenated to gum-stable 100 octane number aviation fuels.

Considerations of the maximum possible conversions obtainable of paraffins to olefines—for polymerization—led to an examination of the possibilities of dehydrogenation. The highest yield of olefines yet produced from butane by pyrolysis is about 60 per cent. by weight, whereas by simple dehydrogenation of butane it should be possible to obtain an olefine yield of 96·5 per cent. by weight consisting entirely of butylenes.

This high yield of olefines from propane or butane is not obtainable in single pass operation, for reasons which are given later, but such a process offers other attractions (*e.g.* production of hydrogen available for hydrogenation). The equilibrium

$$\underset{\text{Paraffin}}{C_nH_{2n+2}} \longrightarrow \underset{\text{Olefine}}{C_nH_{2n}} + \underset{\text{hydrogen}}{H_2}$$

lies well over to the left at temperatures below 350° C., but the extent of dehydrogenation increases with rise in temperature and proceeds extensively above 450° C.

Experiments have been conducted by Frey and Huppke [4] on the dehydrogenation of ethane, propane and the butanes and the equilibrium constants

$$K = \frac{(C_nH_{2n})(H_2)}{(C_nH_{2n+2})}$$

have been determined over the temperature range 350–700° C. These are tabulated in Table VI. From these values of K, the extent of dehydrogenation theoretically possible at various temperatures has been calculated

TABLE VI.

Equilibrium Constants—Dehydrogenation of Paraffins (Frey and Huppke)

($K = \frac{(C_nH_{2n})(H_2)}{(C_nH_{2n+2})}$, concentrations being in atmospheres).

K.	350° C.	400° C.	450° C.	500° C.	550° C.	575° C.	600° C.	650° C.	700° C.
Ethane to ethylene .	—	0·00015	0·00076	0·0032	0·0092	0·017	0·031	0·082	0·20
Propane to propylene	0·00038	0·0022	0·0074	0·027	0·086	0·16	0·24	—	—
n-Butane to 1-butene	0·0045	0·0022	0·0075	0·03	0·095	0·17	—	—	—
n-Butane to *trans*-2-butene . . .	0·00083	0·0039	0·014	0·05	0·16	—	—	—	—
n-Butane to *cis*-2-butene . . .	0·00052	0·0025	0·0087	0·036	0·12	0·20	—	—	—
Total value of K for butane . . .	0·0018	0·0086	0·0302	0·116	0·375	—	—	—	—
*iso*Butane to *iso*butylene . . .	0·0017	0·010	0·042	0·12	—	—	—	—	—

TABLE VII.

Maximum Conversion to Olefines at 350–700° C. from Data of Frey and Huppke.

Percentage Conversion to Olefines (volume).

Hydrocarbon.	350° C.	400° C.	450° C.	500° C.	550° C.	575° C.	600° C.	650° C.	700° C.
Ethane . .	—	1·0	2·8	5·8	9·5	13·0	17·8	28·2	40·8
Propane . .	1·9	4·7	8·7	16·3	28·2	37·0	43·9	—	—
n-Butane . .	3·8	9·4	19·1	32·5	52·3	—	—	—	—
iso-Butane . .	4·2	10·0	20·1	32·8	—	—	—	—	—

and is given in Table VII, whilst the corresponding concentrations of olefines in the exit gases are set out in Table VIII.

Weight conversions to olefines may be obtained from the above table by multiplying by the following correction factors :—

Ethane	0·934
Propane	0·955
n- and *iso*-Butanes	0·966

From the same data the percentage olefines in the exit gases have been calculated and are as given in Table VIII.

TABLE VIII.

Maximum Concentration of Olefines in Exit Gas by Dehydrogenation of Paraffins.

(Olefines % by volume.)

Hydrocarbon.	350° C.	400° C.	450° C.	500° C.	550° C.	575° C.	600° C.	650° C.	700° C.
Ethane	—	1·0	2·7	5·5	8·7	11·5	15·0	22·0	29·0
Propane	1·9	4·5	8·0	14·0	22·0	27·0	30·5	—	—
n-Butane	3·7	8·6	16·0	24·5	34·3	—	—	—	—
iso-Butane	4·0	9·1	16·7	24·7	—	—	—	—	—

In the dehydrogenation of the butanes no molecular rearrangement occurs, according to Frey and Huppke, with the result that *n*-butane yields *n*-butylenes only and *iso*butanes gives exclusively *iso*butylene.

It will be evident from the above figures that it is thermodynamically possible to obtain from normal- or *iso*butane an exit gas containing 30 per cent. of butylene by dehydrogenation at 530° C., the other constituents of the exit gas being 30 per cent. hydrogen and 40 per cent. undecomposed butane. In practice, however, there are various conditions which must be realized before these reactions can proceed satisfactorily. The most important requirement is a suitable catalyst to speed up the dehydrogenation reaction so that it may proceed to a much greater extent than cracking reactions. In the absence of such a catalyst dehydrogenation proceeds to only a slight extent. Other important requirements are complete prevention of any cracking reactions which cause the deposition of cracked products and carbon on the catalyst and so reduce its activity. Polymerization of the olefines formed must also be prevented, because this also causes deposition of products on the catalyst.

The main advantages of dehydrogenation over pyrolysis as a means of producing olefines from paraffin gases for subsequent polymerization are

(1) The lower reaction temperature required (which avoids the use of furnace tubes at temperatures of about 900° C.), and

(2) The smaller loss due to formation of by-products (hydrogen only in the case of dehydrogenation).

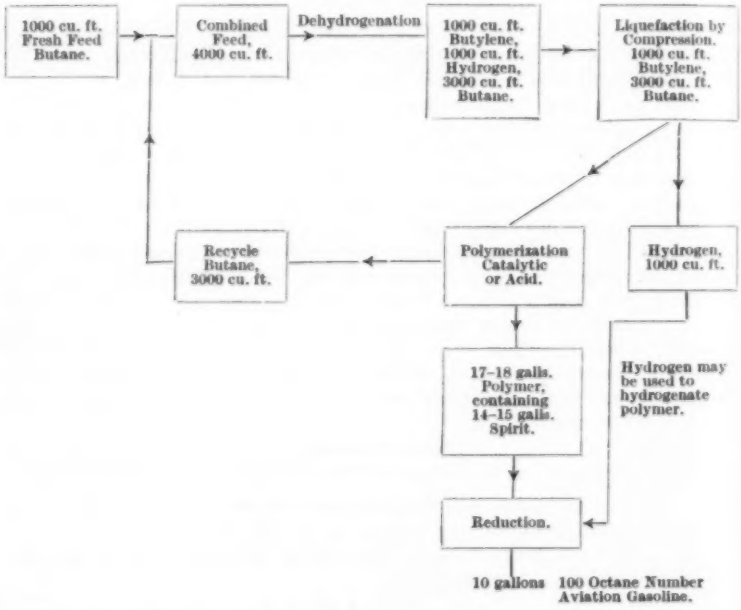
It is of interest to observe that a catalyst capable of continuous operation at 550° C. under equilibrium conditions, gives a conversion of 30 per cent. by weight of butane to butylenes per pass, but even under these conditions a

recycle system is necessary to attain high yields, and means have to be provided for the removal of hydrogen from the recycle gas. Active molybdenum and chromium catalysts examined possess maximum dehydrogenating activity between 450° and 510° C., and the use of higher temperatures causes cracking to occur to an extent sufficient to cause rapid catalyst deterioration.

Large-scale Plant Operation. In large-scale plant operation it is desirable to use conditions giving the highest possible conversion per pass, since this reduces the recycle ratio, and so increases the capacity of any given sized plant. If the maximum conversion per pass obtainable in continuous working is such that the exit gases from the dehydrogenation plant consist of 20 per cent. butylene, 20 per cent. hydrogen and 60 per cent. undecomposed butane the recycle ratio will be 3 to 1. By compression and liquefaction, butane and butylene may be separated from the hydrogen, and the liquid mixture passed to a catalytic or acid polymerization plant, the butylene converted to polymers and the unchanged butane recycled to the dehydrogenation unit. A flow diagram of such a recycle arrangement and the approximate quantities involved, is given in Table IX.

TABLE IX.

Flow Diagram (Ideal Operation).


1000 cu. ft. Fresh Feed Butane.
Combined Feed, 4000 cu. ft.
Dehydrogenation
1000 cu. ft. Butylene, 1000 cu. ft. Hydrogen, 3000 cu. ft. Butane.
Liquefaction by Compression.
1000 cu. ft. Butylene, 3000 cu. ft. Butane.
Recycle Butane, 3000 cu. ft.
Polymerization Catalytic or Acid.
Hydrogen, 1000 cu. ft.
17–18 galls. Polymer, containing 14–15 galls. Spirit.
Hydrogen may be used to hydrogenate polymer.
Reduction.
10 gallons 100 Octane Number Aviation Gasoline.

Results Obtained. The results obtained in single-pass operation in the dehydrogenation of *n*-butane and *iso*butane in small plants are given in

Figs. 7 and 8, and show that equilibrium conditions are obtained at temperatures up to 450–500° C. In general, above this temperature cracking takes place with the formation of methane and ethane, carbon is also deposited.

Under equilibrium conditions the olefines produced from *n*-butane consist almost entirely of *n*-butenes, and *iso*butylene is almost the sole olefine product from *iso*butane. Catalysts comprising the oxides of molybdenum; zinc and magnesium or molybdenum, chromium and magnesium may

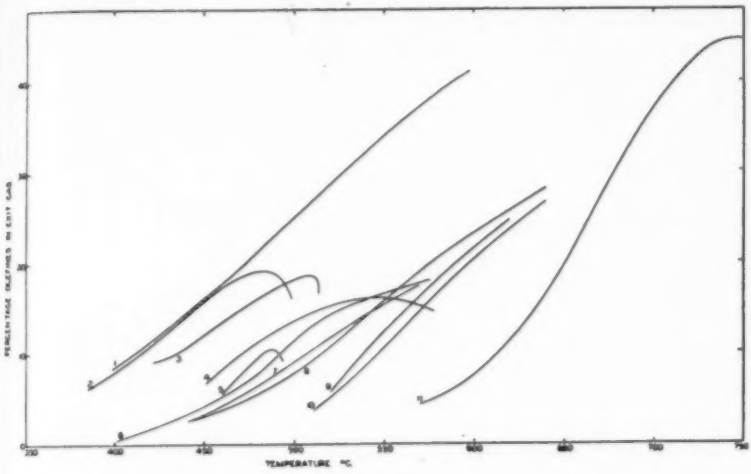


FIG. 7.

DEHYDROGENATION OF NORMAL BUTANE, 97% PURITY.

1. Equilibrium Curve (from Frey and Huppke).
2. Oxides of Molybdenum, Zinc, and Magnesium.
3. Ammonium Chromate on Silica Gel.
4. Ammonium Chromate plus Nitrates of Zinc and Manganese.
5. Titania on Charcoal.
6. Nickel, Alumina and Zinc Oxide on Charcoal.
7. Manganese Nitrate on Charcoal.
8. Copper on Charcoal.
9. Alumina on Charcoal.
10. Active Charcoal.
11. No Catalyst.

readily be regenerated when they have lost activity by oxidation with air at elevated temperatures.

The allowable throughputs of normal- or *iso*butane over effective dehydrogenation catalysts in the temperature range 400–600° C., range from 250 to 2000 volumes per volume of catalyst per hour, the higher throughputs being obtainable with the more active molybdenum and chromium catalysts.

Catalytic Polymerization of Olefines.

Catalytic polymerization was first examined in 1934. A C_4 cut from cracked gas was used as raw material and the effects of a very large number

of neutral salts, acid salts, adsorbents, etc., as catalysts were examined. Parallel with such tests on the commercial mixed olefines tests were made on pure individual olefines to ascertain with more precision the effect of experimental conditions on the rate of polymerization.

Free phosphoric acid (on a charcoal support), certain complex compounds of phosphoric acid with boric acid or with silica, and in particular the acid phosphates of cadmium, were shown to be effective in giving good yields of polymer at temperatures exceptionally low. The high importance of this

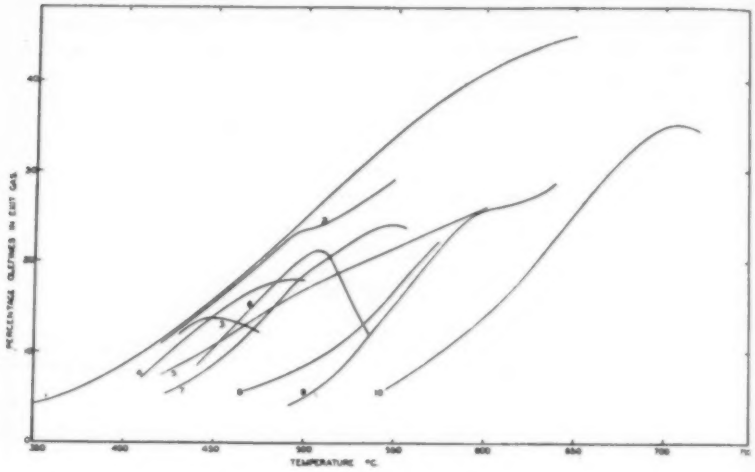


FIG. 8.

DEHYDROGENATION OF *iso*BUTANE.

1. Equilibrium Curve.
2. Ammonium Chromate on Silica Gel.
3. Platinized Asbestos.
4. Ammonium Chromate, Zinc and Manganese Nitrates on Charcoal.
5. Copper Nitrate on Charcoal.
6. Oxides of Cr, Zn and Mo.
7. Oxides of Mo, Zn and Mg.
8. Copper Vanadate on Charcoal.
9. Active Charcoal.
10. No Catalyst.

low temperature lies in the fact that isomerization of the primary polymerization products was reduced, and hence the octane numbers of the final products raised. These tests showed that by catalytic polymerization, 200° E.P. spirits of 78–82 octane number could be produced from the olefines present in cracked gases.

During the course of this investigation, small-scale development work alone involved 20,000 plant hours' operation and over 200 different catalysts were examined.

Details of Plant and Apparatus Employed in Small-scale Development Work. The tests described in this paper have in the main been conducted

in small, continuously operated plants, details of which are shown in Figs. 9–12.

Liquefied cracked gases, and fractions thereof, were stored in large vertical cylinders and fed therefrom to the plants by nitrogen pressure obtained from a nitrogen cylinder. An automatic reducing valve was employed for obtaining constant nitrogen pressure. Ten small plants were employed, nine of which contained a catalyst charge of 100 c.c., and one a catalyst charge of 500 c.c. In addition, preliminary development work was carried out in plants containing up to 30 litres of catalyst. In the original lay-out reflux liquid was fed direct to the top of the reaction tubes, no external preheater being employed. The reaction tubes were

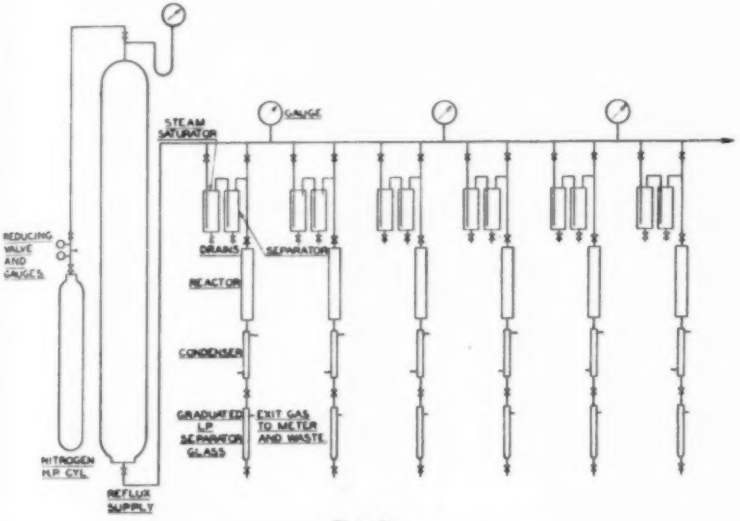


FIG. 9.

LINE DIAGRAM OF BATTERY OF SMALL POLYMERIZATION PLANTS.

electrically heated. After passage over the catalyst the product was cooled under operating pressure in a straight-tube vertical condenser, the pressure released, and polymer product and exit gas separated in a glass receiver at atmospheric pressure. The exit gas was metered and passed to waste.

The reaction tubes were constructed of mild steel 1-in. bore, 1½-in. O.D. and 26-in. effective length. The catalyst was contained in the central portion of the tube, supported on a grid, and a thermopocket reached to the centre of the catalyst. Above the catalyst were placed aluminium Lessing rings to assist vaporization of the feed before passing over the catalyst.

When it was found that admixture of steam with the inlet gas before passage over the catalyst was essential for good results, water saturators and separators were inserted on the inlet lines to the reaction tubes. The saturators, shown in Fig. 11, consisted of small vessels in which the inlet feed was pre-heated to a determined temperature and then bubbled through water

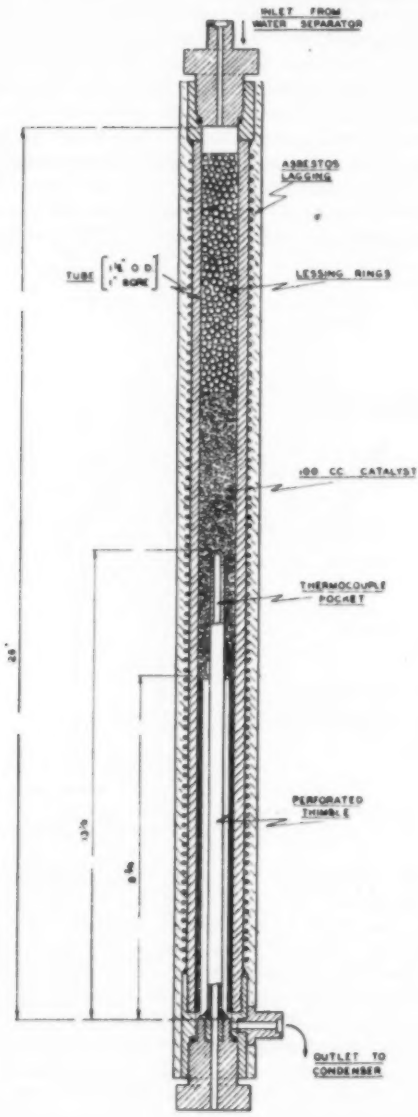


FIG. 10.

ARRANGEMENT OF REACTOR.

maintained at the temperature necessary to give the required degree of saturation. The water separators were found essential, in order to prevent excessive quantities of water being blown over the catalyst during periods of pressure fluctuations and erratic exit gas-rate variations.

A larger plant, of 500 c.c. catalyst capacity, and operated on the same

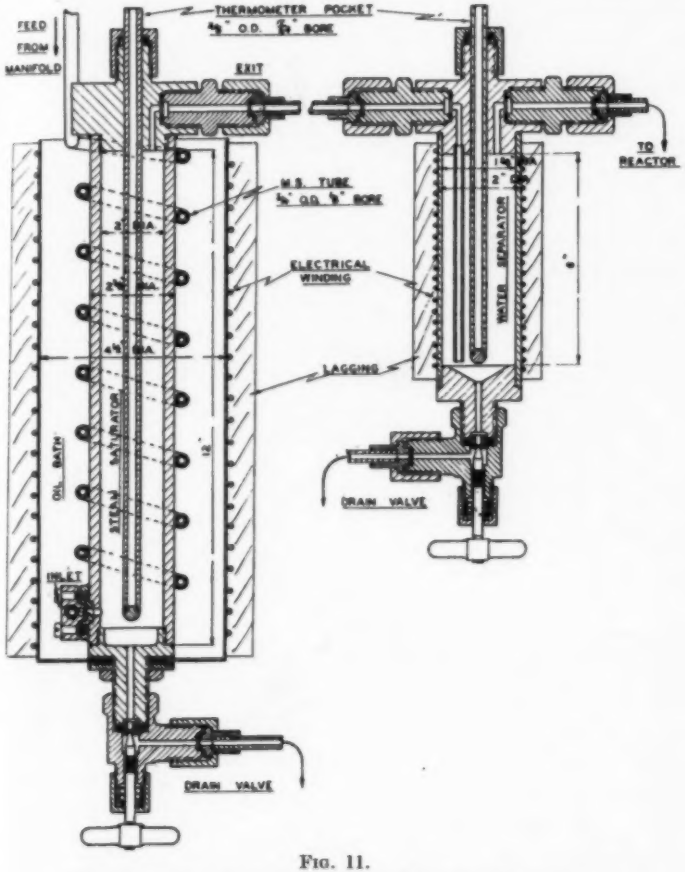


FIG. 11.

ARRANGEMENT OF STEAM SATURATOR AND WATER SEPARATOR.

principle, was also used. This is shown in Fig. 12. In this case an external electrically heated preheater was employed and the reaction tube dimensions were 1¾-in. diameter by 34-in. long.

These plants proved very satisfactory, the only operating difficulty being periodic freezing and choking of the exit valve. With the more robust catalysts this latter trouble disappeared. Photographs of the laboratory plants are reproduced in Figs. 13 and 14.

Methods of Operation. The smaller plants were used for preliminary tests on catalysts, and the conditions were maintained as follows after the effects of the variables had been ascertained :—

Temperature of catalyst . .	230° C.
Pressure	100–150 lb./sq. in.
Catalyst charge	100 ml.
Exit gas rate 10 litres/hour .	measured at approx. 20° C. and 1 atmos. press.

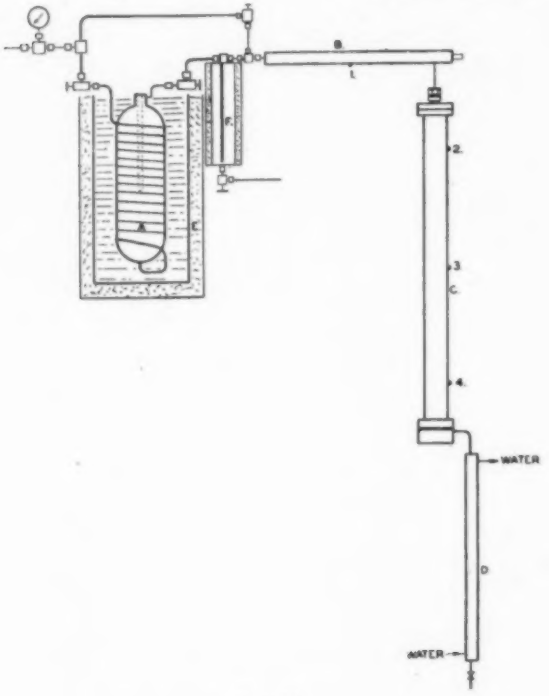


FIG. 12.

LINE DIAGRAM OF CATALYTIC POLYMERIZATION PLANT, 500 C.C. CATALYST CAPACITY.

A. Water Saturator, 5 in. I.D., capacity approx. 1 gall.
B. Preheater, 20 in. × ¼ in. I.D., thermocouple pocket, 15 in.
C. Reactor, 33½ in. × 1¼ in. I.D., capacity 813 c.c.
D. Condenser, 24 in. × 1 in. O.D.
E. Electrically-wound Water Bath.
F. Water Separator.
1, 2, 3, 4. Bugs for Skin Temperature Estimation.

The efficiency of the catalysts examined has been measured in terms of the product produced in tests made under the above standard conditions. More detailed tests, in which catalyst efficiency has been measured in terms

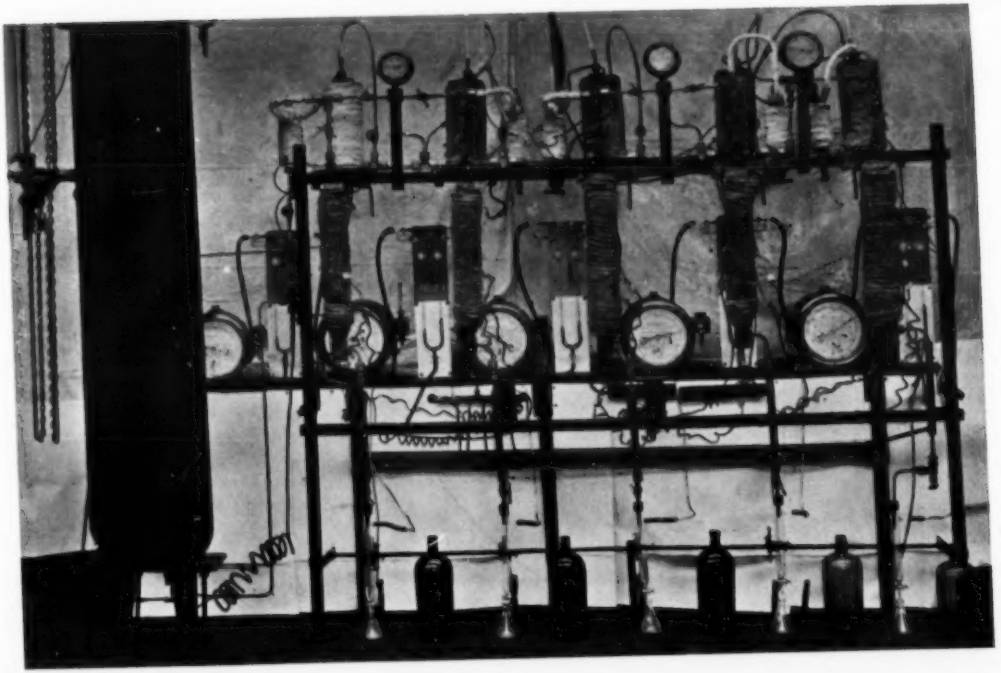


FIG. 13.

EXPERIMENTAL CATALYTIC POLYMERIZATION PLANTS. EACH REACTOR 100 C.C. CATALYST CAPACITY.

[To face p. 368.

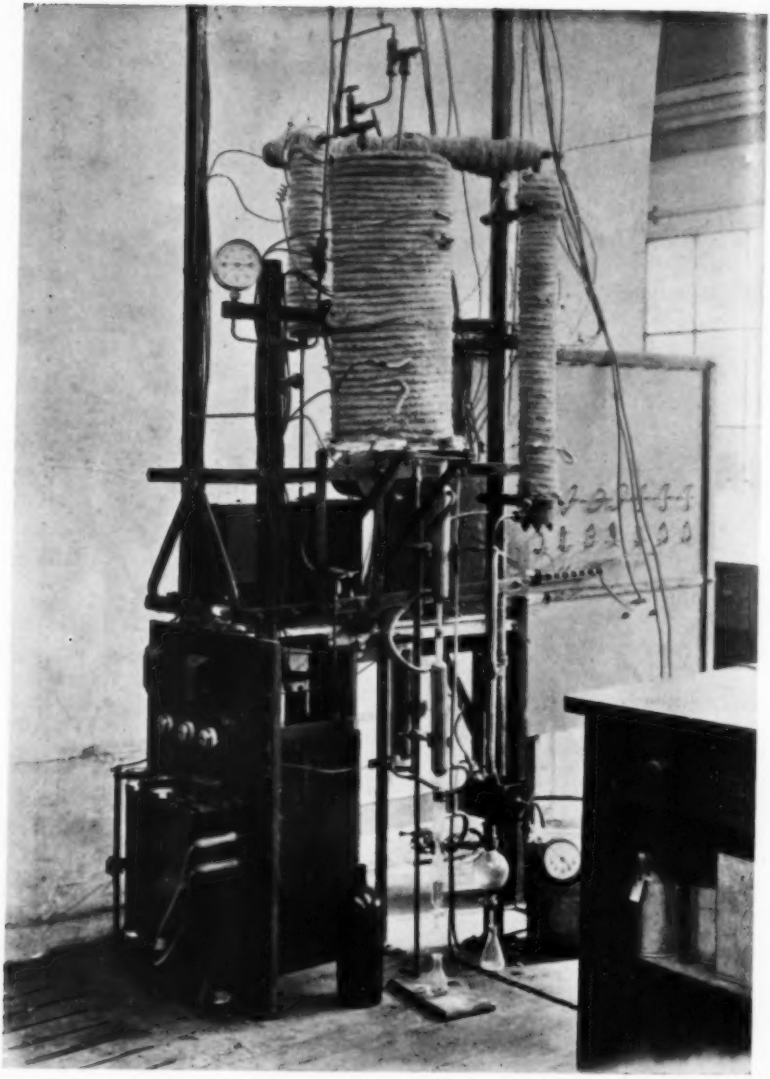


FIG. 14.

EXPERIMENTAL CATALYTIC POLYMERIZATION PLANT, REACTOR CAPACITY, 500 C.C.

of inlet and exit gas analyses, have been made on larger scale plants, which have been continuously operated.

The feed to these small plants was a reflux liquid obtained in the stabilization of cracked gasoline, and had the following average composition, as determined by Podbielniak analysis :—

	% Vol.		% Vol.
CH_4	1·7	C_3H_4	5·8
C_2H_6	5·1	C_3H_6	25·5
C_3H_8	7·4	C_4H_8	45·5
C_4H_{10}	8·6	C_5	0·4

General Considerations. The polymerization process in which a gaseous olefine is converted into an olefine of higher boiling point, whether accomplished with or without a catalyst, involves a decrease in volume of the reactants, and hence is favourably influenced by an increase in working pressure or by an increase in olefine partial pressure. The reaction is also strongly exothermic, the simple reaction

$$iso\text{-}C_4H_8 \longrightarrow iso\text{-}C_8H_{16}$$

involving a heat liberation of approximately 440 B.Th.U./lb. of *iso*butylene reacting. The amount of heat liberated in a commercial process depends on the composition of the olefines polymerized and on the reaction temperature employed, the latter variable determining the extent of secondary isomerization reactions which lead to the formation of non-olefinic products. Nevertheless, no matter what the temperature employed, polymerization is a strongly exothermic reaction, whereas pyrolysis and cracking reactions are endothermic.

In view of the exothermic nature of the polymerization process, it follows that low temperatures should be used for the best results. On the other hand, in order to obtain an adequate speed of reaction, it is essential in most cases to use either a temperature considerably above atmospheric or to employ a catalyst.

In the first case the higher temperatures give a product consisting mainly of isomerization products of the primary olefine polymers, whereas a catalyst permits the use of a temperature sufficiently low to avoid this, and a high-octane-number product results. A further advantage in the use of a catalyst is that much milder conditions of temperature and pressure can be employed, such as 100–300 lb. pressure and 150–300° C. The low pressure is a great advantage, because gases and liquids can be taken to the polymerization plant direct from stabilizers, fractionators and absorbers without the need for pumps or compressors.

Choice of Catalysts. Regarding the choice of suitable polymerization catalysts, many such substances have been known for a long time. The anhydrous metallic halides, such as aluminium and zinc chlorides, are well-known catalysts, but promote isomerization at temperatures as low as − 40° C., and give saturated polymer products of comparatively low anti-knock value.

Bowen and Nash [5] have described tests on the polymerization of ethylene in the presence of aluminium chloride at 150° C. The spirit produced was mainly paraffinic, the fractions having high aniline points and low bromine

numbers, specific gravities and refractive indices, and had an octane number of 73, as determined in the S.30 engine at a jacket temperature of 212° F.

Furthermore, these catalysts form addition compounds with the primary polymerization products, which are corrosive, pasty materials, and very inconvenient to handle. The main use of such catalysts in polymerization is the production of synthetic lubricating oils from cracked distillates and cracked gases. Aluminium and zinc chlorides are not suitable catalysts for the production of high-octane polymer gasolines on a commercial scale.

Boron trifluoride is also a popular polymerization catalyst in the patent literature, but is a most troublesome substance for large-scale use.

Adsorbent materials such as bauxite, fuller's earth, silica and alumina gels, active carbon, refining clays, etc., have also been used as polymerization catalysts for a long time. These substances give polymer products of the desired properties, but suffer from the disadvantage of losing activity in use due to the pores of the catalysts becoming clogged with high-boiling polymers. As far as is known, no commercial plant is yet in operation using any of the above adsorbents as catalysts in the production of anti-knock gasolines from cracked gases.

The action of mineral acids in promoting polymerization is also well known, as, for example, the use of hydrochloric acid as a promoter for silica gel catalysts and the use of sulphuric acid in cracked spirit refining. Sulphuric acid is also used for the production of di*iso*butylene from *iso*-butylene—the reaction proceeding *via* the tertiary butanol stage.

Phosphoric Acid as a Polymerization Catalyst and as an Olefine Direct Hydration Catalyst. In December, 1930, an English patent (340,513) appeared, application date 20.9.29—the first claim of which reads as follows :—

> "A process for the polymerization of lower olefines, which comprises treating the said olefines with catalysts comprising phosphoric acid, meta phosphoric acid or other acids of phosphorus, as such or in the form of their salts and in a solid or solid-like state and operating at temperatures below 400° C."

This patent disclosed the general use of phosphoric acid and phosphates as polymerization catalysts, and mentioned phosphoric acid distributed on active carbons, etc., florida earths and silica gels.

Since the appearance of this patent, there has followed a whole series of patents covering the use of various phosphates as catalysts in the vapour-phase hydration of olefines with steam to the corresponding alcohols. The following is a list of such patents :—

E.P. 369,216. Appl. dates 15.12.30 and 15.9.31.
Catalyst comprising a phosphate of cadmium, beryllium, zinc, aluminium, tin or lead. The preferred composition of cadmium phosphate is $\frac{P_2O_5}{CdO} = 0{\cdot}9$ to 0·725.
Figures are given to show that cadmium phosphate is more active in this reaction than the phosphates of lead, zinc, aluminium or tin.

E.P. 374,510. Appl. date 12.3.31.
A process for removing propylene from crude ethylene mixtures by polymerizing the propylene using cadmium phosphate catalyst.

E.P. 378,865. Appl. date 16.5.31.
Catalytic hydration of olefines using boron phosphate catalyst.

E.P. 392,289. Appl. dates 29.1.32, 10.3.32 and 22.3.32.
Catalytic hydration using phosphates of uranium, iron or cobaltous cobalt—the amount of phosphoric acid being in excess of that required to form the orthophosphate, but not in excess of about 95 per cent. of the composition.

E.P. 392,685. Appl. dates 19.2.32 and 24.2.32.
Catalysts for hydration of olefines—compounded from phosphoric acid and either or both of the metals copper or manganese or their oxides . . ., the amount of phosphoric acid present being in excess of that required to form the orthophosphate but not in excess of about 95 per cent. of the composition.

E.P. 394,389. Appl. date 22.12.31.
Phosphoric acid as a hydration catalyst—initially in the anhydrous condition.

E.P. 396,724. Appl. date 29.1.32.
Boron phosphate as a hydration catalyst. The amount of phosphoric acid being at least 10 per cent. in excess of that required to form the orthophosphate, but not in excess of about 95 per cent. of the composition.

E.P. 403,406. Appl. date 13.6.32.
A motor fuel comprising a mixture of alcohols and hydrocarbon polymers obtained by reacting olefine gas and steam at 200–350° C. in the presence of phosphate catalysts—*e.g.*, boron phosphate.

E.P. 404,115. Appl. date 3.11.32.
Catalysts for hydration reactions—containing a drying oil to improve mechanical strength.

E.P. 407,722. Appl. date 13.9.32.
Alkali and alkaline-earth metaphosphate catalysts.

E.P. 407,944. Appl. date 26.9.32.
Strontium metaphosphate catalyst.

E.P. 408,313. Appl. date 5.10.32.
A catalyst comprising ferric metaphosphate associated with a metaphosphate of a divalent metal—*e.g.* barium, strontium, cadmium, copper or ferrous iron.

E.P. 408,982. Appl. date 18.10.32.
The production of *iso*propyl alcohol using a solid catalyst compounded from phosphoric acid with one or more of the metals manganese, copper, iron, cobalt or uranium with or without boron, or their oxides or compounds, the amount of phosphoric acid being in excess of that required to form the orthophosphates, but not in so great a quantity as to depart from the solid nature of the catalyst.

E.P. 413,043. Appl. date 8.2.33.
A catalyst rendered mechanically stable by incorporating with an organic substance or substances capable of forming true or colloidal solutions in water and which, after subjection to relatively elevated temperatures (of the order of 200° C.) leaves or leave as residue in the catalyst substantially carbon only, *e.g.*, starch, glucose, gelatin, glycerol, etc.

E.P. 415,427. Appl. date 24.1.33.
Catalysts compounded from phosphoric acid with calcium, barium, strontium and/or magnesium oxides—the amount of phosphoric acid being materially in excess of that required to form the orthophosphate, but materially less than that required to form the metaphosphate.

E.P. 415,426. Appl. date 24.1.33.
Catalysts compounded from phosphoric acid with calcium and/or barium and/or strontium, magnesium, the amount of phosphoric acid present being in excess of that required to form the metaphosphates of the elements employed.

E.P. 422,635. Appl. date 24.8.33.
Catalysts rendered mechanically stable by incorporating, during preparation, a non-drying oil such as castor oil, anhydrides, aldehydes, ketones, etc.

E.P. 423,877. Appl. date 11.8.33.
A catalyst consisting of cadmium phosphate together with a small quantity of one or more of the metaphosphates of barium, strontium, titanium, chromium and tellurium.

E.P. 435,769. Appl. date 27.3.34.
Catalysts comprising one or more molecular proportions of aluminium metaphosphate associated with about one molecular proportion of a metaphosphate of calcium, cadmium, zinc, divalent copper, nickel, tin or lead.

The two processes of catalytic hydration and catalytic polymerization of olefines are very similar with regard to catalyst requirements, optimum temperature and influence of pressure, although the products are different. It has been observed many times in the literature that, in the hydration reaction, if the olefine partial pressure or the total working pressure is increased, the rate of alcohol formation is augmented, but polymer formation becomes troublesome, because this also is favourably affected by

increase in pressure. In order to prevent polymer formation and still cause the reaction to occur in the desired direction, it is necessary to increase the partial pressure of the steam and maintain the partial pressure of the olefine at a relatively low value. By this means good yields may be obtained.

The proper choice of catalysts for the vapour phase hydration of olefines under pressure to form alcohols is a very important factor because, as stated by Marek and Hahn [6] in 1932, "catalysts active in promoting the hydration reaction are likewise active toward promotion of the undesirable polymerization reactions, since the latter reaction often proceeds at a more rapid rate."

The following statement is also made by Marek and Hahn:—

> "In contemplating the use of high ratios of steam to olefine in vapour phase hydrations for the purpose of restricting olefine polymerization, sight must not be lost of the fact that excessive steam ratios may impair catalyst activity by flooding the active surface with water molecules. . . . For this reason a mean should be struck between high ratios of steam to prevent polymerization and low ratios to prevent loss of catalyst activity. . . ."

To complete the comparison between polymerization and hydration reactions it is necessary also to consider the reverse of hydration of olefines to alcohols—namely, the dehydration of alcohols to the corresponding olefines.

Phosphoric acid has been used for the preparation of ethylene from ethyl alcohol since this use was first discovered by Pelouzo.[7] In 1933, Lindinger and Moser [8] found that a mixture of alcohol and phosphoric acid would give off ethylene when heated to 205° C. They concluded that the formation of ethylene was due to the action of the pyro acid into which the ortho-acid was being dehydrated, and that a more complete conversion would be obtained at a higher temperature. By passing ethyl alcohol vapour over finely divided pumice soaked in phosphoric acid heated to 250–300° C., a yield of 90 per cent. ethylene was obtained, which was 99·5 per cent. pure. At a later date Newth demonstrated that syrupy phosphoric acid heated previously to 200° C. was more efficient than glacial phosphoric acid (meta-acid) or phosphorus pentoxide. Weber and Walton [9] have concluded that orthophosphoric acid previously heated to 250° C. for 4½ hours gave the best yields of ethylene.

It is thus evident that orthophosphoric acid (containing some pyro acid) is an efficient catalyst for the dehydration of ethyl alcohol to ethylene, and also for the hydration of ethylene to ethyl alcohol. In view of the marked similarities between hydration and polymerization, it is also evident that phosphoric acid should also be a very effective catalyst for the latter reaction—a contention supported by the above-mentioned patents.

The choice of suitable phosphoric acid catalysts for polymerization is also helped somewhat by the above patent specifications. Some of these frequently mention the advantages of catalysts containing free—*i.e.*, uncombined, phosphoric acid, whilst others mostly claim metaphosphates containing, presumably, no free acid. It should be noted here that the hydration reaction is invariably carried out in the presence of large quantities of steam, and that the effective catalysts may actually be ortho-

phosphates, or possibly pyrophosphates or the corresponding acids. The reaction conditions most in favour for the hydration of olefines are as follows:—

Temperature 200–300° C. Pressure atmospheric—2000 lb. Olefine-steam ratios 1 to 1 up to 3 to 1—but at atmospheric pressure may be as high as 10 to 1.

It may thus be expected that under the same conditions—in the absence of steam—polymerization of olefines would proceed at an attractive rate in the presence of a suitable phosphate or phosphoric acid catalyst. As already mentioned, the temperature should be kept as low as possible, to prevent secondary isomerization reactions which lead to the formation of products of inferior knock rating.

Chemical and Physical Properties of Phosphoric Acids. There are many acids of phosphorus—differing widely in their physical and chemical properties—some stable and others either volatile or easily decomposed, and it is necessary, in order to produce a catalyst of long active life and a polymer product free of phosphorus compounds, to choose the particular phosphorus acid with some care.

Fortunately, as shown in Table X, choice is limited to the hydrates of phosphorus pentoxide—namely *ortho-*, *pyro-* and *meta*-phosphoric acids.

TABLE X.

The Acids of Phosphorus.

Name.	Formulæ.	M.pt. (° C.).	Action of heat, etc.
Ortho-phosphoric	$H_3PO_4(P_2O_5–3H_2O)$	36·6–42·5	Dehydrates to mixture of meta and pyrophosphoric acids.
Meta-phosphoric	$HPO_3(P_2O_5–H_2O)$	Sublimes	Polymerizes to give a polymer of lower vapour pressure.
Pyro-phosphoric	$H_4P_2O_7(P_2O_5–2H_2O)$	61	Dehydrates to metaphosphoric acid.
Permono-phosphoric	$H_3P_2O_5$	—	Unstable.
Di-permono-phosphoric	$H_4P_2O_6$		Unstable.
Hypo-phosphoric	$H_4P_2O_6$ or $H_2PO_3(P_2O_4–2H_2O)$	$(H_2PO_3 = 55°$ $+ \frac{1}{2}H_2O = 80°$ $+ H_2O = 70°)$	Phosphine evolved at 180°C. At temperatures above the melting point spontaneously decomposes.
Ortho-phosphorous	$H_3PO_3(P_2O_3–3H_2O)$	70·1–74·0	Evolves phosphine at 140° C.
Meta-phosphorous	HPO_2	—	Reacts with water to form orthophosphorous acid.
Pyro-phosphorous	$H_4P_2O_5(P_2O_3–2H_2O)$	—	Reacts with water to form orthophosphorous acid. Decomposes at 130° C.
Hypo-phosphorous	H_3PO_2	17·4–26·5	Evolves phosphine at 100° C.

Of these the former is a regular article of commerce, and is cheaper than the pyro acid—whilst the *meta*-acid is inactive catalytically (see later).

The most suitable phosphoric acid to employ is therefore *ortho*phosphoric

acid, which may be obtained in the anhydrous state, in 50 per cent. or in 90 per cent. solutions in water.

The presence of phosphorus pentoxide in polymerization catalysts is precluded because this substance sublimes at 180–250° C. and its vapour pressure may reach 760 mm. at 250° C. At higher temperatures, however, polymerization of the oxide causes the vapour pressure to fall considerably. Phosphorus trioxide is of little use, because it boils at 173° C. at 760 mm. pressure, whilst phosphorus tetroxide sublimes at about 180° C.

As shown in Table X, *ortho*phosphoric acid is dehydrated by the action of

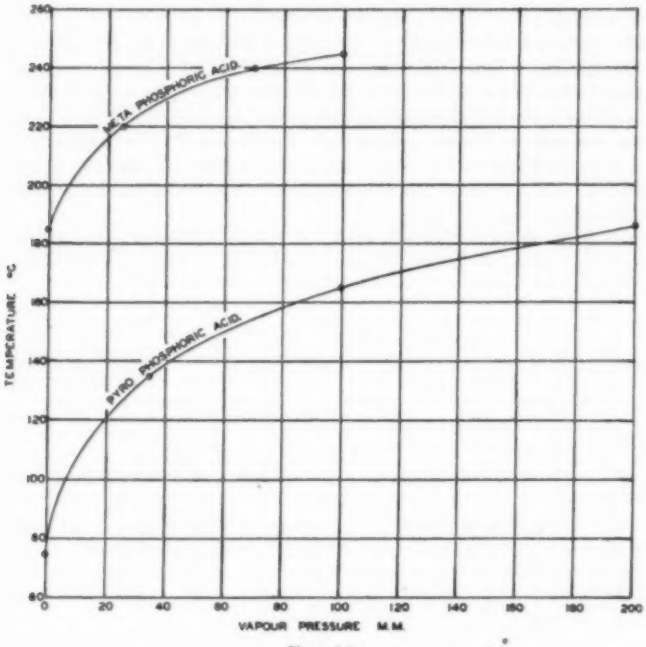


FIG. 15.

VAPOUR PRESSURES OF PHOSPHORIC ACIDS.

heat to give both *pyro* and *meta* acids, both of which are much too volatile for commercial use. The dehydration of *ortho*-phosphoric acid may be briefly summarized as follows:

When a dilute solution of orthophosphoric acid is evaporated at temperatures up to 150° C., a syrupy liquid is obtained which consists entirely of orthophosphoric acid and between 150° and 160° C. it loses water slowly. At 240° C. orthophosphoric acid loses water so that the ratio P_2O_5/H_2O = 1 : 2⅔–1 : 2½—as compared with 1 : 3 for pure ortho-acid. At higher temperatures more water is liberated until a product is obtained consisting mainly of metaphosphoric acid. The literature is not conclusive regarding the minimum temperatures required for the formation of pyro- and meta-

acids, but it is generally supposed that the conversion to pyrophosphoric acid is not complete at 230° C.—whereas it is so at 260° C., and that meta-acid begins to form at about 290° C. It is most probable that, during the dehydration of orthophosphoric acid, there is a state of equilibrium between the three acids—dependent on the temperature and the partial pressure of any water present. Thus dehydration is greatly suppressed by the presence of water vapour. A consequence of dehydration is the formation of lower acids more volatile than the original ortho-acid—as shown in Fig. 15. Therefore, if dehydration is allowed to occur—greater loss of acid—due to volatility, might be expected, although experimental evidence is at variance with this deduction to some extent.

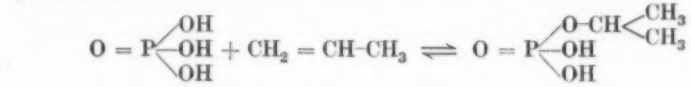
Prevention of Phosphoric Acid Dehydration. At the outset of this work it was observed that although catalysts prepared from either ortho- or pyro-phosphoric acid are active catalytically, catalysts prepared from meta-phosphoric acid possess no activity. This is mentioned later, with regard to active carbon catalysts and also kieselguhr catalysts. Further important observations were the rapid decline of the activity of all phosphoric acid catalysts in use, and the fact that all such used catalysts contained meta-acid. These observations showed that, as was to be expected from the above comments on dehydration, the cause of catalyst decline was the formation of meta-acid, and the obvious way to prevent this was the admixture of small quantities of water vapour in the gas before passage over the catalyst. In this way it is possible to keep the water content of the catalyst substantially constant, the amount of water mixed with the inlet gas just compensating that lost from the catalyst by dehydration. The amount of water required is approximately 2–10 per cent. by volume of the inlet feed, the water being measured in the form of steam. By injecting water or steam in this way catalyst deterioration by the formation of meta-acid is prevented. The amount of water should not exceed the above limits, otherwise alcohol formation is appreciable and often the mechanical strength of the catalyst is impaired.

With catalysts of high free acid content dehydration leads to the formation of large quantities of meta-acid, which change the catalyst from a hard cake to a wet pasty mass. The use of steam to prevent acid dehydration is not novel; the scheme was suggested in E.P. 368,051 (March 3, 1932) for maintaining sulphuric acid catalysts at a constant strength at 140–160° C.

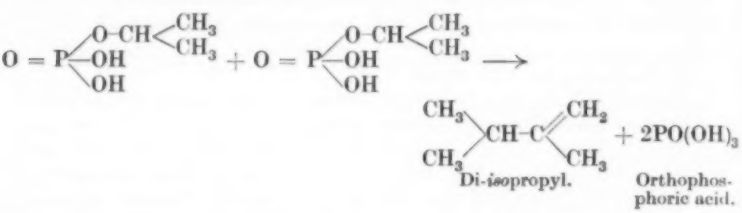
The effect of steam admixture with the inlet gas on catalyst life and activity is dealt with later in the separate sections devoted to each class of catalyst examined.

Formation of Volatile Phosphorus Compounds. A further consideration with regard to the use of phosphoric acid as a polymerization catalyst is the possibility of the formation of volatile compounds by interaction of the phosphoric acid with the olefines being treated. This undoubtedly occurs with some phosphoric acid catalysts—particularly with catalysts consisting of phosphoric acid impregnated active carbons and has also been observed by Sanders and Dodge [10] in the dehydration of ethyl alcohol to ethylene using phosphoric acid as catalyst at 300° C. In this connection the mechanism of polymerization suggested by Ipatieff [11] has a direct bearing. Ipatieff postulates the formation of intermediate alkyl phosphates which break down again as soon as formed.

E.g., in the case of propylene, *iso*propyl phosphate is supposed to be formed—thus



which decomposes as follows :—



Ipatieff has demonstrated that when propylene is heated with phosphoric acid a homogeneous liquid is formed which contains esters such as the above, and that the liquid, on subsequent heating, liberates hydrocarbon polymers. It is believed that some such intermediates must be formed. When a phosphoric acid-active carbon catalyst is employed for the polymerization of olefines in the presence of small amounts of added steam, to prevent dehydration, the condensed water contains a little free phosphoric acid and a considerable quantity of combined phosphoric acid.

Alkyl phosphates are volatile compounds as shown by the following figures :—

Dimethyl ethyl phosphate . .	B. pt. 203·3° C.	at 760 mm.
Methyl diethyl phosphate . .	,, 208·2° C.	,,
Triethyl phosphate . . .	,, 215–216° C.	,,
Tripropyl phosphate . . .	,, 138° C.	at 47 mm.
Tri-*iso*propyl phosphate . .	,, 218–220° C.	at 763 mm.
Tri*iso*butyl phosphate . .	,, 135–136° C.	at 8–10 mm.

Experience indicates that loss of phosphoric acid from catalysts—presumably due to the formation of volatile phosphorus compounds—is more pronounced in the case of catalysts comprising phosphoric acid on inert carriers such as active carbon or coke than with other catalysts. Furthermore, loss of phosphoric acid occurs only when the concentration of phosphoric acid on the inactive support is above 20 per cent. (This is more fully dealt with later.)

Reactions between Phosphoric Acid and Metal Oxides, etc.—Of the various materials commonly used in catalyst masses only carbons and cokes have been found unreactive with phosphoric acids at temperatures up to 300° C., although even in the case of these substances there is the remote possibility of reduction of the phosphoric acid to phosphine, especially if the carbon or coke contains any oxides, such as ferric oxide.

When any other materials, such as oxides, aluminates, silicates, carbonates, etc., are mixed with phosphoric acid and heated to give a hard mass, chemical reactions occur to give phosphates. This even takes place in the

case of silica, and in this case compounds of the type $(SiO_2)_x(P_2O_5)_y$ are formed—these are probably silicyl phosphates and are very stable towards heat.

The literature evidence for the formation of stable compounds between siliceous materials and phosphoric acid is as follows :—

1. Phosphoric acid has practically no effect on glass at ordinary temperatures, but at 100–150° C. the attack is marked and silicyl phosphate and metaphosphates are produced.[12] At 400° C. phosphoric acid has a strong corrosive action on quartz glass.[13]

2. When a dried mixture of gelatinous silica and metaphosphoric acid is fused and extracted with hot water, transparent crystals are obtained, the composition of which corresponds to SiO_2–P_2O_5, which has been considered to be silicyl metaphosphate—$SiO(PO_3)_2$.[14]

3. Silica *dissolves* in orthophosphoric acid, and forms crystals of the composition SiO_2–P_2O_5.

Silicates and aluminates react with phosphoric acid as mixtures of the corresponding oxides and gives mixed phosphates; examples of such silicates are pumice and floridin.

The work described in this paper leads to the conclusion that the catalytic activity of all phosphate catalysts is greatly affected by the presence of free phosphoric acid—probably in the ortho condition. Therefore, unless the acid is present in a quantity more than sufficient completely to combine with the support under the reaction conditions of temperature and water vapour pressure, an inactive, or only weakly active, catalyst is obtained. On the other hand, the catalyst activity is to a large extent dependent upon the composition of the phosphates present, some being practically ineffective and others very efficient.

There is, of course, a very definite upper limit to the amount of phosphoric acid which can be incorporated in a catalyst suitable for commercial use. As the amount of acid is increased the hardness of the catalyst diminishes, and a definite limit to the acid content is imposed for this reason. In the case of some catalysts, however, total acid contents as high as 75–80 per cent. can be tolerated.

Regeneration of Used Phosphoric Acid Catalysts. In use all phosphoric acid or phosphate catalysts become clogged with volatile high-boiling polymers, which if allowed to stay on the catalyst cause the latter to become disintegrated and very soft. In addition to this volatile material there is also formed on the catalyst a fairly large amount of practically non-volatile asphalt-like material which causes the catalyst volume to increase and also causes caking. This latter material is not so deleterious in its effect as the former, but at least partial removal is necessary after the catalysts have been in use for prolonged periods. A small amount of asphaltic material on the catalyst is beneficial in giving the catalyst greater activity and a higher degree of mechanical strength.

The first step in any regeneration is the removal of the volatile high-boiling polymers which tend to disintegrate the catalyst, and this is readily accomplished by flushing with a stream of nitrogen or flue gas at 300° C. for 4–12 hours. When asphaltic material has accumulated, this can only be removed by treatment with flue gas containing small amounts of oxygen

—at temperatures up to 350° C. In this manner the asphaltic material is removed by oxidation or partial combustion. Care is necessary in this step to prevent the development of local hot spots in the catalyst—otherwise acid is lost by volatilization.

With regard to the first step, we have found that this is applicable to many types of phosphate catalyst and is very effective when performed after each 100 hours' catalyst use, although this time interval may be much prolonged if necessary. If this is done there is no need to burn off any asphaltic material for over 1500 hours' catalyst life.

Details of catalyst regenerations are given later.

Phosphoric Acid—Active Carbon and Other Similar Catalysts.

As already shown, phosphoric acid reacts chemically with all siliceous and aluminous materials, and also with nearly all metal oxides and with silicates and aluminates. On the other hand, at the temperatures employed in the process, 90 or 100 per cent. phosphoric acid cannot react with carbon. Thus active carbons and various cokes are unique in one important respect that they are truly inactive supports, and are therefore of especial interest.

Active carbons vary widely with regard to their adsorptive powers for 90 per cent. phosphoric acid, but the grade used in the present work adsorbs up to 50 per cent. by weight of this material, and in so doing does not lose its hard granular structure. The catalyst can be rendered quite dry and free flowing by drying at 200–230° C. for 24 hours. Its bulk density (when containing 45 per cent. by weight of H_3PO_4) is 0·8–0·85.

Tests have shown that shale coke (obtained in the coking distillation of shale oil), sized to 4–10 mesh, is a suitable support and will adsorb up to 45 per cent. by weight of 90 per cent. phosphoric acid. Shale coke suffers some disintegration after impregnation, however, and the dried catalyst is not so hard as a comparable active carbon catalyst. This disadvantage may be overcome by limiting the amount of phosphoric acid adsorbed.

The following catalysts, prepared from phosphoric acid and 4–10 mesh active carbon are of interest :—

1. Active carbon containing *ca.* 45 per cent. H_3PO_4. Dried at 200–230° C. for 24 hours before use.
2. Active carbon containing *ca.* 20 per cent. H_3PO_4. Dried at 250° C. for 24 hours before use.
3. Active carbon containing *ca.* 45 per cent. pyrophosphoric acid ($H_4P_2O_7$).
4. Active carbon containing *ca.* 45 per cent. metaphosphoric acid (HPO_3).
5. Active carbon containing *ca.* 50 per cent. orthophosphoric acid, 0·9 per cent. cadmium and 0·7 per cent. copper, these metals being present in the form of phosphates.
6. Active carbon containing *ca.* 40 per cent. orthophosphoric acid and 0·8 per cent. silver sulphate.

The results obtained on these catalysts are detailed in Tables XI and XII.

TABLE XI.

Summary of Tests on Phosphoric Acid-Active Carbon Catalysts.

(100 c.c. Catalyst and 10 litre/hour Exit Gas Rate in each case.)

Cat. no.	Run no.	Temp. ° C.	Pressure lb./sq. in.	% Steam in inlet feed. (vol.).	Water separator in use?	Duration. Hours.	Product. c.c.	Product / Catalyst Weight ratio.	Product grm./hour per 100 grm. cat.	Comments.
1	51	230	90–120	nil	no	59	753	7·6	12·9	Catalyst in very good condition.
1	55	230	120–80	nil	no	235	2318	19·45	8·3	" " "
1	122	230	150	17	no	204	3286	27·8	13·6	Catalyst in excellent condition.
1	123	230	150	17	no	203	3441	27·8	13·7	" " "
1	149	230	100–150	6–9	no	262	2606	28·0	10·7	" " "
1	169	230	150	6	no	103	918	10·0	9·8	" " "
6	192	230	160	6	no	72	1446	13	18·0	" " "
2	107	230	150	7	yes, after 30 hr.	132	2822	29·8	22·6	" " "
3	194	230	160	6	no	120	2112	16·7	13·9	Water ceased after 87 hrs.
4	201	230	150	7	no	18	19	0·245	1·36	Catalyst inactive.
5	208	230	150–160	6	no	80	2380	19·8	24·8	Catalyst treated at 300° C. for 4 hrs. with nitrogen *in situ*. In excellent condition.

The catalyst used in Run 122 was treated with nitrogen at 300° C. for 70 hours and then used in Run 149.
The catalyst after use in Run 149 was treated for 7 hours at 300–400° C. with nitrogen *in situ* and then used in Run 169.

TABLE XII.

Analyses of Used and Unused Phosphoric Acid-Active Carbon Catalysts.

Run no.	Cat. no.	Free acid content of catalyst.		Total H_3PO_4 content of catalyst. % weight.		H_3PO_4 in catalyst. Grm.		H_3PO_4 in product Grm.	H_3PO_4 in water. Grm.	Loss of H_3PO_4 in run. Grm.	Comments.
		Initial.	Final.	Initial.	Final.	Initial.	Final.				
51	1	29	11	46·5	31·0	34·3	22·9	—	nil	—	No steam in inlet feed.
55	1	29	12·7	46·5	29·7	41·8	26·7	—	nil	—	" "
122	1	29	10·0	46·5	36·6	41·3	34	nil	0·12	—	Catalyst regenerated and used in Run 149. Excessive water in product.
123	1	29	7·0	46·5	25·0	43	23·3	nil	0·31	19·39	Excessive water in product.
149	1	7·0	—	25·0	—	17	—	trace	trace	1·3	Catalyst regenerated and used in Run 169.
169	1	—	6·5	—	22·9–23·4	—	15·7	trace			Catalyst used after regeneration from Run 149. No water separator.
192	6	20	trace	38·1	9·6–10·0	31·6	8·12	trace	11·75	11·73	Excessive water at 30 hrs.
197	2	7·2	6·5	22·7–23·1	28·7	16·3	14·9	trace	0·107	nil	Steam separator in use after 37 hrs.
194	3	21	1·5	49·8–53·8	17·3–18	49·0	16·8	trace	4·64	27·6	Water in product ceased after 87 hrs. No water separator.
201	4	11·7	8·6–10·0	53·1	39·9–39·2	30·8	23·0	—	—	—	—
208	5	17·5	7·2	53·25	29·5	47·9	26·5	trace	3·52	17·88	No water separator.

The following points are important :—

1. Runs 51 and 55 were made with no steam mixed with the inlet feed. This explains the rapid rate of catalyst deterioration.
2. Runs 122 and 123 were made using 17 per cent. steam in the inlet feed.
3. Runs 149 and 169, made on regenerated catalysts, were conducted using a normal amount of steam (6–9 per cent. vol.) in the inlet feed.
4. Run 197, made on a carbon catalyst containing a smaller quantity of phosphoric acid, was conducted using 7 per cent. steam in the inlet feed, and a water separator was also installed to prevent excess water being carried on to the catalyst.
5. Runs 192, 194, 201 and 208 were conducted with 6–7 per cent. steam in the inlet gas (a normal quantity), but no water separators were in use.

It will be observed that except in the case of Run 197, considerable losses of phosphoric acid were observed. This was probably due to one or both of the following causes :—

1. Washing effect of steam in the inlet gas. When water separators were not employed, fluctuations in the exit gas rate often caused excessive quantities of water to be carried over from the vaporizer to the catalyst in the reactor.
2. Probably the concentration of phosphoric acid in No. 1 catalyst (45 per cent. by weight) is too high.

It should be noted that in Run 197, where no appreciable loss of phosphoric acid was observed, a water separator was employed, and the catalyst (No. 2) contained only 23 per cent. of phosphoric acid. In this run no appreciable loss of catalytic activity was observed.

Also, in Runs 149 and 169 made with the same batch of catalyst used in Run 123 the loss of acid was very small—only 0·7 grm.—a quantity within the limit of experimental error. In these runs no steam separator was in use, but the catalyst contained only 34 per cent. phosphoric acid.

Tests in which phosphoric acid-active carbon catalysts have been exposed for prolonged periods at 300° C. to the action of a stream of nitrogen or nitrogen containing 20 per cent. steam, have shown that under these conditions the loss of phosphoric acid is small, despite the high vapour pressure of metaphosphoric acid. The results of such tests are as follows :—

Test no.	Catalyst.	Gas.	Temp. (° C.).	Duration (hrs.).	Total phosphate content of catalyst (% weight).	
					Initial.	Final.
R. 36	Fresh No. 1	Nitrogen	300	74	46·5	50·3
R. 37	,,	Nitrogen + 20% steam	300	71·5	46·5	41·6 and 40·7
R. 43	No. 1 ex Run 123	,,	300	70	25·4	22·0, 23·0, 24·0

A further quantitative test demonstrated that after exposure to a current of nitrogen for 16 hours at 300° C., the loss in weight was only 7·7 per cent., the first 19 hours giving 6·4 per cent. loss in weight, presumably due to loss of water from the catalyst.

Catalyst No. 5 contains 0·9 per cent. cadmium and 0·7 per cent. copper—both in the form of phosphates—in addition to 53 per cent. total phosphoric acid, but it is doubtful if the phosphate additions have any beneficial effect. The same remark applies to the small silver sulphate content of catalyst No. 6.

Summarizing these points, it appears therefore that in phosphoric acid-active carbon catalysts the amount of phosphoric acid present should be limited to a figure of approximately 30 per cent. by weight, and the amount of steam in the inlet gas should be limited to 7 per cent. by volume. Unless these precautions are taken, acid is lost from the catalyst and corrosion will become evident.

Work carried out on much larger plants on phosphoric acid-active carbon catalysts containing 45 per cent. by weight of phosphoric acid has shown that the loss of acid from the catalyst is not serious when careful control of operating conditions is exercised, but catalyst deterioration is evident to a marked degree.

Cadmium Phosphate Catalysts.

As already mentioned, cadmium phosphate was the first phosphate polymerization catalyst examined in the present investigation. Preliminary tests in continuous plants showed that it was very active, and sufficiently attractive for large-scale use, provided its activity could be maintained for long periods and provided it could be obtained in a form possessing the requisite mechanical strength and resistance to disintegration during use.

A cadmium phosphate of the composition $Cd(PO_3)_2$ or $Cd(H_2PO_4)_2$ is more active than the normal orthophosphate $Cd_3(PO_4)_2$. The former phosphate was prepared by mixing the orthophosphate and orthophosphoric acid in the proportions corresponding with

$$Cd_3(PO_4)_2 + 4H_3PO_4$$

and was first of all employed in the granular form (10–20 mesh), either with or without an equal volume of pumice of the same mesh added. (Catalysts 7 and 8 respectively.)

In an experimental plant using a reactor of 9 litres capacity, a temperature of 200° C., a pressure of 180 lb. and an inlet feed of 4 cu. ft. of stabilizer reflux per lb. of No. 7 catalyst per hour, the initial conversion of inlet olefines to polymers was 54 per cent., but this rapidly decreased until a conversion of only 16·5 per cent. was realized after 230 hours' operation.

In the above tests no steam was mixed with the inlet feed. Tests in small continuous laboratory plants of 100-c.c. catalyst capacity also showed that this catalyst quickly loses its activity in use when no steam is present in the inlet feed, and showed that this loss of activity was associated with a loss in the free acid content of the catalyst.

The results obtained on this catalyst in these small plants were as follows :—

Run no.	Temp. ° C.	Press. Lb./sq. in.	Wt. of cat. Grm.	Product. c.c.	Product / Cat.	Product. Grm./100 g. cat./ Hr.	Free acid content of cat.		Product c.c./hr. 12-hourly periods.						
							Initial.	Final.	12.	24.	36.	48.	60.	72.	84.
1	230	110– 90	78	926·5	8·9	22·2	20	2·4	43	25·8	7·5	—	—	—	—
8	200	140–100	81·4	150·8	13·8	16·2	20	2·8	41	24·7	22·5	15	11·3	6·7	4

and show that the rate of catalyst deterioration is greater in the small laboratory plants than in the larger plant, and that it is greater at 230° C. than at 200° C.

It should be noted that No. 7 catalyst contains only 50 per cent. by weight of active material—the pumice being a diluent.

Due to the unsuitable mechanical strength of No. 7 catalyst and the ease with which it became clogged in use, attempts were made to make acid cadmium phosphate in a more rugged form. Using a pelleting machine, acid cadmium phosphate of the composition $Cd_3(PO_4)_2 + 4H_3PO_4$ was made into pellets approximately 3 × 5 mm. (No. 9), which were of much greater mechanical strength than the catalyst of the same composition in granular form (No. 8). Five per cent. of graphite was added to the phosphate before pelleting to act as a die lubricant. The pelleted catalyst was examined in the small laboratory plants both with and without steam present in the inlet feed, with the results given in Table XIII.

In the tests in which steam was mixed with the inlet feed, high conversions were maintained for 200–300 hours, but after use the catalyst was in poor condition unless it was treated with nitrogen for 4 hours at 300° C., in which case the catalyst was recovered in its original pelleted form—the used pellets being black and dry and very hard. It is evident that the reaction conditions are such as to make large demands on the mechanical strength of the catalyst. A further observation of interest was that the total H_3PO_4 contents of used No. 9 catalysts from Runs 135 and 140 were the same as that of the unused catalyst—within small limits—indicating that no appreciable quantity of phosphoric acid is lost from the catalyst in use.

Attempts were then made to increase the initial hardness of pelleted acid cadmium phosphate by the admixture of other substances. It was also hoped that some catalyst-promoting effect might also be observed. The following catalysts were therefore pelleted :—

No.	Per cent.			Per cent.	
10	97·2	acid cadmium	phosphate	+ 2·8	zinc oxide.
11	60·5	,,	,,	+39·5	phosphomolybdic acid.
12	97	,,	,,	+ 3	manganese dioxide.
13	97·2	,,	,,	+ 2·8	copper oxide.
14	80	,,	,,	+20	stannic oxide.
14	50	,,	,,	+50	copper phosphate.
16	80	,,	,,	+20	calcium phosphate.
17	80	,,	,,	+20	calcium sulphate.
18	80	,,	,,	+20	quick lime.
19	80	,,	,,	+20	stannous phosphate.

TABLE XIII.

Run no.	Temp. ° C.	Press. Lb./sq. in.	Per cent. steam in inlet feed. Vol.	Product. C.c.	Product / catalyst Wt.	Product. Grm./100 g. cat./ Hr.	Duration of runs. Hrs.	Per cent. free acid. Fresh cat.	Per cent. free acid. Used cat.	Appearance of used catalyst.
11	200	120–110	nil	2771	14·5	11·4	127·5	24	14 (meta)	—
12	200	120–110	,,	2621	13·7	11·6	118·5	—	—	—
14	150	140–130	,,	580	3·15	3·13	100·5	—	—	—
16	175	170–120	,,	1557	8·44	3·97	212·5	24	15	Soft, brown-black.
93	230	75–110	,,	2429	14·2	7·9	178	—	12·8	Very bad condition. Black, sticky.
71	230	70–100	*ca.* 12·5	9560	50·2	14·3	352	22	—	Black.
72	230	70–100	*ca.* 12·5	4415	22·9	16·4	139·5	22	12·9	Choke caused shut down.
135	200	150	*ca.* 7–17·0	3404	18·2	9·7	187	21·5	16	After blowing with N_2 at 300° C. 4 hrs. Dry, black and fairly hard.
140	230	150	*ca.* 7–17·0	4966	26·7	11·2	238	21·5	11	,, ,, ,,
147	230	150	*ca.* 6·5	3650	18·9	20·5	92	24	15·9	Black, slightly soft, but suitable for further use.

Total Phosphate content unused No. 9 Catalyst = 57%
,, ,, ,, after Run 135 = 56·6%
,, ,, ,, ,, ,, 140 = 55·2%

Of these, Nos. 15, 16, 17, 18 and 19 were harder than normal. These catalysts were examined in small laboratory plants, but in no case were the used catalysts improvements on used pelleted acid cadmium phosphate catalyst.

Effect of Organic Binding Agents. Numerous references are made in the literature to the effect that the addition of various organic substances to phosphate catalysts improves mechanical strength, *e.g.* :—

E.P. 404,115. 3.11.32.

Incorporation with a drying oil in the catalyst—followed by heat treatment—*e.g.* linseed oil or tung oil.

E.P. 413,043. 8.2.33.

Incorporation with an organic substance capable of forming true or colloidal solutions in water and which leave a carbonaceous residue on heating, *e.g.* starch, sucrose, carbohydrates, glucose, molasses, gelatine, glycol, etc.

E.P. 422,635. 24.8.33.

Incorporation with a non-drying oil, *e.g.* castor or rape oil, cetyl alcohol, ethers, ketones, anhydrides, aldehydes, etc.

Various attempts have been made to improve catalyst ruggedness by incorporating such materials as those mentioned above, with the following results :—

Linseed Oil. No. 20. An intimate mixture of 97 per cent. acid cadmium phosphate ($Cd_3(PO_4)_2 + 4H_3PO_4$) and 3 per cent. linseed oil was prepared and baked at 200–250° C. for 44 hours. Pungent vapours were evolved, and a black, dry, powdery mass resulted. This was then pelleted and gave hard pellets—a very decided improvement on normal acid cadmium phosphate.

The hardness was further improved by baking at 300° C. for 70 hours. This treatment reduced the free acid content to 2·8 per cent.

Tung Oil. No. 21. An intimate mixture of 95 per cent. acid cadmium phosphate and 5 per cent. tung oil was heated at 250° C. for 70 hours. The resulting black, dry, friable mass was ground and sieved, mixed with 5 per cent. of graphite and pelleted. The pellets were very soft.

No. 22. A similar result was obtained on a mixture of 90 per cent. acid cadmium phosphate and 10 per cent. tung oil.

No. 23. A mixture of 80 per cent. acid cadmium phosphate and 20 per cent. tung oil was heated at 250° C. for 48 hours. The resulting black, dry, friable mass was ground and sieved, baked a further 2 hours at 250° C. to remove a little remaining moisture, 5 per cent. graphite added and the mixture pelleted. The pellets were very soft.

Heating the pellets to 250° C. for 45 hours effected considerable improvement, but completely satisfactory pellets were not obtained.

Sugar. No. 24. A mixture of 90 per cent. acid cadmium phosphate + 10 per cent. sugar was heated to 250° C. for 46 hours, ground, sieved, mixed with 5 per cent. graphite and pelleted. The resulting pellets were very soft.

Gelatin. No. 25. 95 per cent. acid cadmium phosphate + 5 per cent. gelatin. (Gelatin powder was used dissolved in hot water.) The mixture failed to dry after 117 hours at 250° C. followed by 147 hours at 300° C.

Tricresyl Phosphate. No. 26. 90 per cent. acid cadmium phosphate + 10 per cent. tricresyl phosphate. Heated to 250° C. for 186 hours and then pelleted. Pellets unsatisfactory.

Triphenyl Phosphate. No. 27. 90 per cent. acid cadmium phosphate + 10 per cent. triphenyl phosphate. Heated to 250° C. for 23 hours and then pelleted. Pellets soft.

Petroleum Pitch (m.pt. 213–215° F.). No. 28. A mixture of 90 per cent. acid cadmium phosphate and 10 per cent. of finely ground petroleum pitch was heated at 250° C. for 41 hours, sieved, mixed with 5 per cent. graphite and pelleted. The resulting pellets were very poor.

Acid Tar. No. 29. Acid tar obtained in the acid refining of lubricating oil was heated to 50° C., and was added to acid cadmium phosphate in an amount

equal to 10 per cent. by weight of the total mixture. The mixture was heated to 250° C. for 65 hours—ground and sieved, heated to 250° C. for a further 3 hours, mixed with 5 per cent. graphite and pelleted. The pellets obtained were quite good. The hardness was considerably improved by heating the pellets to 250° C. for 43 hours—when the free acid content fell to 9·5 per cent.

No. 30. A mixture of 5 per cent. acid tar and 95 per cent. acid cadmium phosphate was incorporated, sieved and pelleted without any prior heat treatment. The pellets so obtained were very hard. These were then baked at 250° C. for 17 hours, and became *exceptionally hard* (free acid content 8 per cent.).

A further batch of pellets baked at 250° C. for 64 hours was also *exceptionally hard* and contained 2 per cent. free acid.

No. 31. A mixture with acid cadmium phosphate containing 2½ per cent. of acid tar was mixed and pelleted. Again very good pellets were produced, which on baking at 250° C. for 23 hours became exceptionally hard.

It will be seen that the most satisfactory results are obtained when the binding agent is added to the catalyst before the drying prior to pelleting, this necessitating the use of small amounts of binding agent, since otherwise

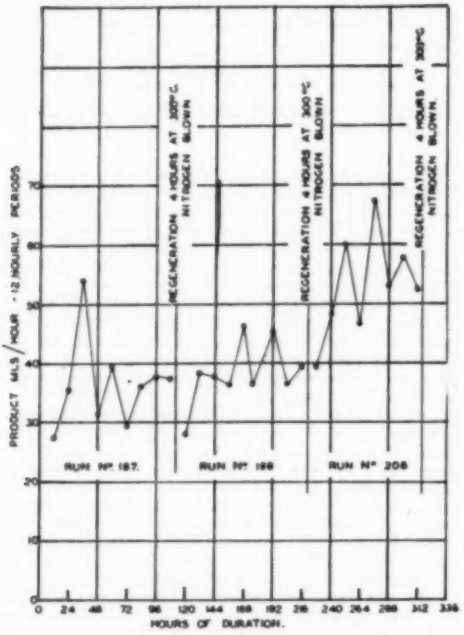

PRODUCT MLS/HOUR - 12 HOURLY PERIODS
REGENERATION 4 HOURS AT 302°C NITROGEN BLOWN
REGENERATION 4 HOURS AT 300°C NITROGEN BLOWN
REGENERATION 4 HOURS AT 302°C NITROGEN BLOWN
RUN Nº 187.
RUN Nº 199
RUN Nº 206
0 24 48 72 96 120 144 168 192 216 240 264 288 312 336
HOURS OF DURATION.

FIG. 16.

TESTS ON CADMIUM PHOSPHATE–ACID TAR CATALYST (NO. 31). YIELD OF PRODUCT REDUCED TO A COMMON BASIS OF 100 GRM. CATALYST CHARGE.

Run no.	Duration, hours.	Product / Catalyst	Product, grm./hr. per 100 grm. catalyst.
187	112	30·4	27·0
199	110	32·8	29·8
206	95	37·8	39·8
	317	101·0	

TABLE XIV.

Results of Tests on Catalysts comprising Acid Cadmium Phosphate plus Organic Binding Agents.

TABLE XIV.

Results of Tests on Catalysts comprising Acid Cadmium Phosphate plus Organic Binding Agents.

Cat. no.	Run no.	Temp. ° C.	Press. lb./sq. in.	% Steam in inlet gas % Vol.	Duration. Hrs.	Product. c.c.	Product Catalyst weight ratio.	Product. Grs./100 g. cat./hr.	Free acid content of catalyst %		Total H_3PO_4 content of catalyst weight.		Comments.
									Initial.	Final.	Initial.	Final.	
29	143	230	150–100	30–11	184	5506	36·2	19·8	10	15·2	—	—	Loss in activity due to a choke. Catalyst black.
30	152	230	150	*ca.* 7	183	6001	47·3	25·6	8	13·7	60·5	—	Catalyst in good shape.
31	155	230	150	*ca.* 7	144·5	22217	26·9	18·6	4	14	61·4	58·4	Shut down due to choke and excessive water in feed. Catalyst caked and soft.
31	182	230	150	*ca.* 7	68·5	3131	19·2	28	4	14·5	61·4	60·6	Pellets in original form. Became very hard on heating at 300° C.
31	187	230	150–160	*ca.* 7	112	5087	30·4	27	—	5	61·4	—	Catalyst treated *in situ* with nitrogen at 300° C. for 4 hrs. Very hard, in excellent condition—used in Run 199.
31 ex Run 187	199	230	150	*ca.* 7	110	5109	32·8	29·8	—	5	—	54	Catalyst treated *in situ* with nitrogen at 300° C. for 4 hrs. Very hard, in excellent condition—used in Run 206.
31 ex Run 199	206	230	150	*ca.* 7	95	3942	37·8	39·8	—	1·0	54	58·1	Catalyst treated *in situ* with nitrogen at 300° C. for 4 hrs. Very hard, in excellent condition.
31	204	260	150	*ca.* 7	85	3769	26·2	30·8	—	trace	61·4	59·4	Catalyst treated *in situ* with nitrogen at 300° C. for 4 hrs. Catalyst hard but caked in part. Not in such good condition as after use at 230° C.

satisfactory pelleting is impossible. Used under these conditions, acid tar from the treatment of lubricating oil is a good binding agent.

Tests on acid cadmium phosphate–acid tar catalysts are detailed in Table XIV. Very satisfactory results were obtained when treatment with nitrogen at 300° C. was employed after 100 hours' running. In this way, three 100-hour tests were made on one batch of No. 31 catalyst, nitrogen treatment being given after each 100 hours, and the catalyst, after this use, was in excellent condition and, if anything, harder than initially. In these three runs the total quantity of polymer produced from one charge of catalyst was 14,138 c.c., equivalent to a product/catalyst ratio of 101, and an average rate of product formation of 32·2 grm. product per 100 grm. of catalyst per hour.

Furthermore, the used catalyst contained 58·1 per cent. total H_3PO_4, whereas initially it contained 61·4 per cent. total H_3PO_4. These figures show that the loss of phosphoric acid from the catalyst is small.

The results obtained in the above three successive runs on this catalyst are shown in Fig. 16, in which the product makes have been adjusted to a common basis of 100-grm. catalyst charge. It will be noticed that no catalyst deterioration is evident.

Effect of various Heat Treatments on Acid Cadmium Phosphate Catalysts. The amount of free titratable phosphoric acid in an acid cadmium phosphate catalyst is no index to its catalytic activity. This is evident from the above results obtained on regenerated No. 31 catalysts, and also from the following figures :—

A sample of pelleted acid cadmium phosphate of the composition $Cd_3(PO_4)_2 + 4H_3PO_4$, of 57 per cent. total H_3PO_4 and 23 per cent. free acid content was heated in an oven for 72 hours at 300° C., and then for 70 hours at 230° C. in a current of nitrogen containing 10 per cent. steam. After this treatment the total H_3PO_4 content of the catalyst was 55·4 per cent., but the free acid content was reduced to 1·1 per cent. (No. 9–R31).

The two catalysts, of negligible free acid content, were, however, just as active as the same catalysts prior to heat treatments and containing 20–30 per cent. free acid, as shown in the following figures :—

	No. 9–R. 31.
Run no.	*106*
Temperature (° C.)	230
Pressure (lb./sq. in.)	70–150
Percentage steam in inlet feed (vol.)	25–12
Product (c.c.)	8027
Product/catalyst	93
Product (grms./hr./100 grm. catalyst)	39·2

There is thus no danger in heating acid cadmium phosphate catalysts for prolonged periods at 300° C., even though metaphosphate formation must be appreciable under these conditions.

Effect of Acid Content.

Acid Cadmium Phosphate Catalysts containing Smaller Amounts of Phosphoric Acid.

The acid cadmium phosphate referred to above had the composition $Cd(H_2PO_4)_2$ or $Cd_3(PO_4)_2 + 4H_3PO_4$. It was considered that catalysts

TABLE XV.

Acid Cadmium Phosphate Catalysts containing less than 4 moles of Phosphoric Acid per mole of Cadmium Orthophosphate.

Catalyst no.	Composition.	Per cent. added H_3PO_4 in mixture.	Time and Temperature of drying.	Mole ratio $\frac{P_2O_5}{CdO}$	Per cent. free acid (analysis)	Per cent. total H_3PO_4 (analysis)	Comments.
No. 32	$Cd_3(PO_4)_2 + 2H_3PO_4$	27	12 hr. 100° C.	0·66	6–7	50·3	Very hard pellets.
„ 33	$Cd_3(PO_4)_2 + 2{\cdot}5H_3PO_4$	32	20 hr. 250° C.	0·75	7	53·3	Hard pellets.
„ 34	$Cd_3(PO_4)_2 + 3H_3PO_4$	36	20 hr. 100° C.	0·83	15	55·0	Very hard pellets.
„ 35	$Cd_3(PO_4)_2 + 3{\cdot}5H_3PO_4$	40	20 hr. 100° C.	0·92	20	—	Very hard pellets.

TABLE XVI.

Results obtained on Acid Cadmium Phosphate Catalysts containing less than 4 moles H_3PO_4 per mole Cadmium Orthophosphate.

Catalyst no.	34	34 ex Run 185	34 ex Run 198
Run no.	185	198	207
Temperature (° C.)	230	230	230
Pressure (lb./sq. in.)	160	160	150–160
Per cent. steam in inlet gas (% vol.)	6	6	6–7
Product (c.c.)	5867	4489	2977
Product/catalyst (wt.)	32·5	28	22·8
Product (grm./hr./100 grm. cat.)	23·7	24·8	25·4
Duration (hr.)	137	112	90
Product (c.c./hr.). *12-hourly periods.*			
12 hr.	40	40	29
24 „	47·4	37	29
36 „	61·4	57	26
48 „	54	46	47
60 „	49	43·4	37
72 „	47	39	34·5
84 „	36·5	34·6	38
96 „	39	34·7	—
108 „	32	30·5	—
120 „	33·4	—	—
132 „	35	—	—
Free acid content of catalyst. (%) Initial	15	trace	1·5
Final	trace	1·5	1·5
Total H_3PO_4 content of catalyst. (%) Initial	55	57·8	57
Final	57·8	57·0	55·2
Comments	Catalysts treated *in situ* with N_2 4 hr. at 300° C. Very hard pellets. Excellent condition	Catalysts treated *in situ* with N_2 4 hr. at 300° C. Used catalyst in excellent condition. Used in Run 207.	

of greater mechanical strength, although probably of lower activity, could be obtained by reducing the amount of phosphoric acid in the initial mixture. The catalysts detailed in Table XV were thus prepared. The method of preparation was very simple, and consisted in mixing cadmium orthophosphate and 90 per cent. orthophosphoric acid in the required proportions, a little water being added if necessary in order to get a uniform stiff paste. This paste was then dried for 12–20 hours in a steam oven and gave a hard mass which was broken up, sieved, granulated and pelleted. The initial mixtures of cadmium orthophosphate and phosphoric acid quickly set hard on standing or on heating to 100° C.

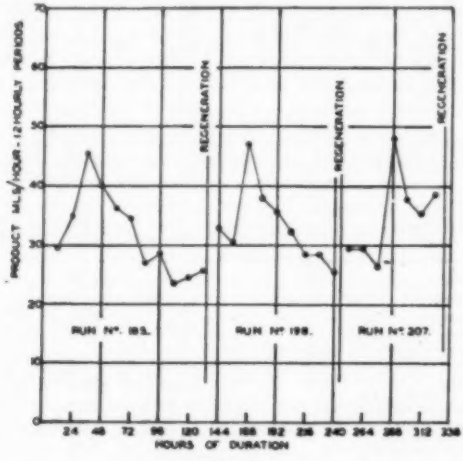


FIG. 17.

TESTS ON CADMIUM PHOSPHATE CATALYST (NO. 34). YIELD OF PRODUCT REDUCED TO A COMMON BASIS OF 100 GRM. CATALYST CHARGE.

Run no.	Duration, hours.	Product Catalyst	Product, grm./hr. per 100 grm. catalyst.
185	137	32·5	23·7
198	112	28·0	24·8
207	90	22·8	25·4
	339	83·3	

This method of catalyst preparation offers considerable advantages for large-scale use.

The results obtained on these catalysts are detailed in Table XVI, and show that the material of empirical composition $Cd_3(PO_4)_2 + 3H_3PO_4$ is a very satisfactory catalyst if regenerated by nitrogen treatment after each 100 hours' use.

In Runs 185, 198 and 207, which were made on the same 100 c.c. sample of catalyst, the total product make was 13,333 c.c., equivalent to a product/catalyst ratio of 83·3, and an overall rate of product formation of 24·6 grm. per 100 grm. of catalyst per hour.

These figures show that this is slightly less active than a catalyst which contains 4 moles of H_3PO_4 per mole of cadmium orthophosphate.

Fig. 17 shows that no catalyst deterioration is evident in the three runs—185, 198 and 207, whilst the analytical figures given in Table XVI show that the total phosphoric acid content of the catalyst after 339 hours' operation was the same as initially—*i.e.* the catalyst does not lose phosphoric acid in use.

This same catalyst has been used in a semi-scale plant for periods up to 1500 hours without any evidence of deterioration in catalytic activity.

Cadmium Phosphate Catalysts prepared from Cadmium Oxide and Phosphoric Acid.

Various mixtures of cadmium oxide and 90 per cent. phosphoric acid were made up as follows:—

TABLE XVII.

Cadmium Phosphate Catalysts prepared from Cadmium Oxide and 90 per cent. Phosphoric Acid.

Catalyst no.	Per cent. H_3PO_4 in initial mixture.	Mole ratio $\frac{P_2O_5}{CdO}$.	Time and temperature of drying. (hr.)	(° C.)	Free acid (%).	Appearance of catalyst.
36	43·0	0·5	48	200	nil	Fairly hard.
37	51·0	0·67	48	200	nil	Fairly hard.
38	53·8	0·75	48	200	16·0	Soft.
39	60·9	1·0	43	240	5·5	Powdery mass.
40	67·1	1·33	173	250	18·3	Fairly hard—hygroscopic.
41	70·0	1·5	100	300	—	Wet sticky mass—not usable.
42	75·2	2·0	100	300	—	Wet sticky mass—not usable.

None of these mixtures gave hard catalysts, numbers 36 and 37 being the most satisfactory in this respect, but both of these were inactive catalytically. For an active and usable catalyst, *i.e.* one containing free acid, the mole ratio $\frac{P_2O_5}{CdO}$ should be between 0·67 and 1·5—*i.e.* the H_3PO_4 content should be between 51 and 70 per cent. Catalysts containing less acid are inactive, whilst those containing more acid cannot be satisfactorily dried.

The results show that the mole ratio $\frac{P_2O_5}{CdO}$ must be higher in the above catalysts than in cadmium orthophosphate–phosphoric acid mixtures for comparable catalytic activity. The above catalysts are more difficult to prepare than the latter, and are not very hard.

Mixed Phosphate Catalysts containing Cadmium.

Cadmium phosphate is an expensive material, and various attempts have been made to reduce the cost of finished cadmium catalysts by incorporating cheap ingredients which have some other desirable property such as hardness.

(a) *Mixtures of Phosphoric Acid with Cadmium Oxide, Copper Oxide and Bauxite or Alumina.*

Mixtures of these ingredients are excellent from the point of view of hardness, but the catalysts examined have fairly low activities.

(b) *Mixtures of Cadmium Oxide, Phosphoric Acid and Pumice.*

These mixtures are also very hard, probably the hardest yet prepared, and are also active catalytically.

Catalysts prepared from Cadmium Phosphate, Copper Phosphate and Phosphoric Acid, and from Cadmium Phosphate, Aluminium Phosphate and Phosphoric Acid.

Because of the superiority of cadmium phosphate catalysts prepared from the orthophosphate and phosphoric acid over those made by the calcination of mixtures of cadmium oxide and phosphoric acid, it was decided to prepare mixed phosphate catalysts comprising cadmium–copper and cadmium–aluminium by the first procedure. The orthophosphates were intimately mixed in powder form, the requisite amount of 90 per cent. phosphoric acid added and the resulting pastes dried at 100° C. Some of the catalysts prepared are listed in Table XVIII.

TABLE XVIII.

Cadmium–Copper and Cadmium–Aluminium Catalysts prepared from the Orthophosphates and Phosphoric Acid.

Catalyst no.	Composition.	Time and temperature of drying.	Free acid (%).	Total H_3PO_4 content % (analysis).	Appearance, etc.
43	$Cd_3(PO_4)_2$–$Cu_3(PO_4)_2$–H_3PO_4 = 1 : 1 : 2	100° C. 18·5 hr.	4–5	54·7	Hard granules and pellets.
44	do. = 1 : 1 : 4	100° C. 12 hr.	10–11	58·5	do.
45	do. = 1 : 1 : 6	100° C. 47 hr.	18–19	66	Reasonable pellets.
46	$Cd_3(PO_4)_2$–$AlPO_4$–H_3PO_4 = 1 : 1 : 2	100° C. 24 hr.	nil	—	Good pellets.
47	do. = 1 : 1 : 4	100° C. 24 hr.	13–14	—	do.
48	do. = 1 : 1 : 6	100° C. 48 hr.	25	69·5	do.
49	do. = 1 : 1 : 3	100° C. 40 hr.	10·9	59·25	Granules powder easily. Friable.

The copper–cadmium mixtures were very hard after drying, and could be disintegrated into very hard blue granules. When pelleted, the resulting pellets were very hard. The cadmium–aluminium mixtures were rather less hard.

Results obtained on these catalysts are detailed in Table XIX, and show that the former catalysts are sufficiently active to be attractive, and may be fully regenerated after 100 hours' use by flushing with nitrogen at 300° C. for 4 hours. This is also shown in Fig. 18.

TABLE XIX.

Tests on Cadmium–Copper and Cadmium–Aluminium Catalysts.

Cat. no.	43	43	43	43	44	44	44	49	49	49	44	45	45	48	44
Run no.	161	173	165	178	162	166	170	167	172	164	190	196	193	203	205
Temperature (° C.)	230	230	230	230	230	230	230	230	230	230	230	230	230	230	23,230
Pressure (lb./sq. in.)	150	150	150	150	150	140–150	150	150	150	150	150	150	150	150	150
Percentage steam in inlet gas	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Product (c.c.)	6,411	2,166	5,703	2,029	2,824	14,147	576	521	418	625	215	2,304	4,928	4,176	3,002
Product/catalyst (wt.)	38·5	13	32·9	12·2	20·8	95	6·7	4·2	3·4	5·9	0·99	10·5	32	25·6	32·1
Prod. (grm./hr./100 g. cat.)	21·4	15	21·8	12·7	33	30·3	22·6	6·2	5·8	6·2	5·5	7·4	27·8	27·7	37·5
Duration (hr.)	180	86·5	151	96·5	63	313	30	68	58	95	18	142	115	93	86
Free acid content of Catalyst (%). Initial	4·5	4·5	4·5	4·5	11	11	11	11	—	11	—	18·6	—	25	—
Final	—	—	—	—	18	—	3	—	< 1	2·5	—	—	5·2	3·2	2·6
Total H_3PO_4 (%). Initial	54·7	54·7	54·7	—	58·5	58·5	—	59·25	59·25	59·25	—	66	—	69·5	—
Final	—	53·5	—	54·5	—	53	—	—	—	56	—	—	58·6	70·2	57·9
Appearance of used catalyst	Treated with N_2, 300° C. 4 hr. *in situ*, then used in Run 173.	Dry, caked, friable.	Treated with N_2, 300° C. 4 hr. *in situ*, then used in Run 178.	Black, hard and dry.	Black.	Black, dry. Fairly good condition.	Black, dry. Excessive steam.	Treated with N_2, 300° C. 4 hr., then used in Run 172.	Black, hard and dry.	Dry and hard.	Treated with nitrogen 3 hr. at 300° C. Very hard and dry.		Black, hard and dry. Good condition after treating with N_2, 4 hr. at 300° C.	Black, hard and dry.	Black, hard and dry. Good condition after treating with nitrogen 4 hr. at 300° C.

In Runs 193 and 205, made on the same 100-c.c. batch of No. 44 catalyst (used in granular form), the total product make was 7930 c.c., equivalent to a $\frac{\text{Product}}{\text{Catalyst}}$ ratio of 64·2 and an average ratio of product formation of 32·7 grm. per 100 grm. of catalyst per hour. These results are slightly better than the best obtained on the cadmium phosphate catalysts Nos. 31 and 34.

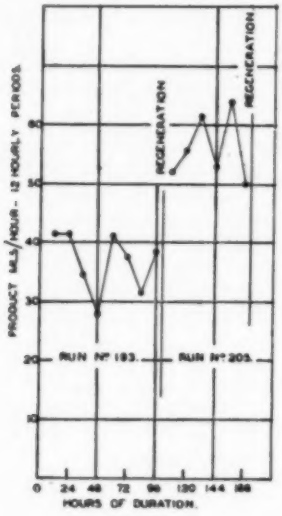


FIG. 18.

TESTS ON CADMIUM PHOSPHATE–COPPER PHOSPHATE CATALYST (NO. 44 GRANULAR). YIELD OF PRODUCT REDUCED TO A COMMON BASIS OF 100 GRM. CATALYST CHARGE.

Run no.	Duration, hours.	$\frac{\text{Product}}{\text{Catalyst}}$	Product, grm./hr. per 100 grm. catalyst.
193	115	32	27·8
205	86	32·1	37·5
	201	64·1	

The results given in Table XIX also reveal that the catalytic activities of

No. 44. $Cd_3(PO_4)_2$–$Cu_3(PO_4)_2$–H_3PO_4 = 1 : 1 : 4

and

No. 48. $Cd_3(PO_4)_2$–$AlPO_4$–H_3PO_4 = 1 : 1 : 6

are roughly equal. This shows that for the same acid concentration, the presence of aluminium lowers the activity. On the other hand, the figures given above show that the addition of copper increases the catalytic effect of cadmium.

Mixtures of Cadmium Phosphate, Copper Phosphate and Phosphoric Acid containing various Cements, etc.

Attempts to improve the already good mechanical strength of copper-cadmium catalysts prepared from the orthophosphates have not been

very satisfactory, because in each case the additions have proved deleterious. This applies to plaster of Paris, sodium silicate and other similar substances. The addition of kieselguhr causes a marked decrease in hardness.

General Considerations on Cadmium Phosphate Catalysts.

A number of the above catalysts are fully suitable for large-scale use. Their catalytic activity is high, and they retain their mechanical strength in a very satisfactory manner—in fact, in each case the hardness of the catalyst improves in use. Each of these catalysts is easily prepared. Tests on larger scale plants have shown that such catalysts may be used for periods in excess of 1500 hours without suffering any loss in activity.

Kieselguhr and Silica Phosphoric Acid Catalysts.

These catalysts have the advantage of being cheap and easily prepared, but they are hygroscopic and have considerably less mechanical strength than those described above.

Throughout the work described in this paper, acid washed kieselguhr was employed. This was a fine white powder which analysed as follows :—

Loss on ignition	10 per cent.
Silica	86 „
Magnesium oxide	2 „
Iron and Aluminium oxides	0·4 „
Moisture	5·5 „

The first kieselguhr catalysts prepared were various mixtures with 90 per cent. phosphoric acid, to determine the maximum amount of acid which could be used and to determine what conditions of drying, etc., were necessary. The following mixtures were thus prepared :—

No. 50	Kieselguhr/phosphoric acid	=	35/65	(90	per cent. acid)
„ 51	„	„	= 50/50	(„	„)
„ 52	„	„	= 18/82	(„	„)
„ 53	„	„	= 35/65	(100 „	„)
„ 54	„	„	= 28/72	(90 „	„)
„ 55	„	„	= 18/82	(100 „	„)

Of these catalysts No. 51, after drying at 250° C. for 2 hours, consisted of a hygroscopic light brown powder which showed no sign of caking. This showed that the amount of acid incorporated must be greater than 50 per cent. When the acid content of the initial mixture was 65 per cent., as in No. 50, a light brown pasty mass was obtained, which on drying at 250° C. for 6 hours set into a soft cake which was easily broken up. Increasing the acid content to 82 per cent., as in No. 52, necessitated much longer drying, *e.g.* 30 hours at 250° C., and the final mass was, if anything, rather softer than No. 50. Catalysts 55, 53 and 54 closely resembled No. 50.

It was observed that the temperature of drying of kieselguhr catalysts had a pronounced effect on the free acid content. This is shown in the following figures which refer to a 65/35 phosphoric acid–kieselguhr mixture :—

Temperature of drying (° C.).	Time of drying (hr.).	Per cent. free H_3PO_4 in dried catalyst.
300	50–60	1·0 (meta acid)
250	24	9·5
190–200	94	63·0

In each case the time of drying was that required to give a hard product, except in the case of that prepared at 300° C., when the drying time was purposely prolonged to determine its effect. The latter mixture, which contains only 1 per cent. of free acid, approximates in composition to SiP_2O_7 or $SiO_2(PO_3)_2$.

A marked reduction in free acid content also occurs when either of these kieselguhr catalysts is used in polymerization at 200–230° C. in the absence of added steam. On the other hand, in the presence of the optimum amount of steam no such reduction in free acid content occurs. The loss in free acid content is not associated with a loss in total H_3PO_4 content, and is solely caused by further reaction of the acid with the kieselguhr support—probably higher phosphates are formed. A further interesting point is that if a kieselguhr catalyst of appreciable free acid content, *e.g.* 30 per cent., is heated to 300° C. until the free acid content is negligible, hydrolysis cannot be effected by subsequent treatment with superheated steam at 300° C., or with nitrogen containing up to 20 per cent. steam at the same temperature. To effect hydrolysis the temperature must not be above 200° C.

On the other hand, if a No. 52 catalyst, previously heated at 300° C. to reduce the free acid content to zero, is used for the polymerization of olefines at 230° C. in the presence of small amounts of water vapour—then hydrolysis takes place in a few hours, giving a catalyst of 20–30 per cent. free acid content.

A catalyst (No. 56) was also prepared by the repeated impregnation of kieselguhr with 90 per cent. phosphoric acid, as follows :—

650 grm. of kieselguhr was mixed with 350 grm. of phosphoric acid, 260 ml. of distilled water were added to give a thick cream and the whole was dried at 180–190° C. for 18 hours. At this stage the free acid content was 34 per cent. The mixture was then powdered and dried at 300° C. for 18 hours—the free acid decreasing to 0·9 per cent. The powdered material was then mixed with 700 grm. of 90 per cent. H_3PO_4 and 100–150 c.c. water and dried at 180–200° C. for 18 hours and then at 250–260° C. for 18 hours. After this treatment the catalyst was a fairly hard white mass of 32 per cent. free acid content.

This catalyst was prepared at the outset of this programme of experimental work, when the reasons for decrease in free acid content on heating and in use in the absence of steam were not fully understood. It was thought at that time that such decrease in free acid content might be prevented by incorporating a large excess of acid in the catalyst before use. In the light of present knowledge catalyst No. 52 is quite as satisfactory as No. 56, and is, of course, much more easily and cheaply prepared.

An attempt was made to reduce the reactivity of kieselguhr with phosphoric acid by roasting it in a muffle furnace at 1000° C. for 24 hours. This roasted kieselguhr was then mixed with 100 per cent. H_3PO_4 in the proportions 18/82 by weight and dried at 240° C. for 167·5 hours (No. 57). A comparison of this catalyst with a No. 55 catalyst prepared under identical conditions from unroasted kieselguhr is as follows :—

	No. 55.	No. 57.
Free acid content . .	29·6%	37·0%
Appearance . . .	Soft and hygroscopic.	Soft, but harder than No. 55.

There is thus a definite advantage in using kieselguhr previously roasted to 1000° C.

Catalysts prepared by roasting mixtures of metaphosphoric acid and kieselguhr are much harder than the corresponding mixtures with orthophosphoric acid, but are inactive.

No. 58 catalyst was prepared by drying a mixture of 85 per cent. meta-acid and 15 per cent. kieselguhr for 17 hours at 250° C. followed by 77 hours at 300° C. The resulting catalyst was very hard and dirty white in colour.

A mixture of H_3PO_4, zinc chloride and kieselguhr in the weight proportions 75/10/15, dried at 250° C. for 42½ hours, gave a product of similar appearance and hardness to No. 52, of 30 per cent. free acid content.

Silica gel was used in the preparation of catalyst No. 59. A mixture of 51·5 per cent. silica gel and 48·5 per cent. H_3PO_4 (90 per cent. strength) was

TABLE XX.

Kieselguhr and Silica–Phosphoric Acid Catalysts.

Cat. no.	Composition.	Mole ratio P_2O_5. SiO_2	Time and temperature of drying.	Free acid (%).	Appearance and comments.
50	H_3PO_4 on kieselguhr: 65% of 90% acid	0·57	Various	8–60	Soft, easily broken up.
51	H_3PO_4 on kieselguhr: 50% of 90% acid	0·28	250° C. 2 hr.	—	Moist: hygroscopic powder, non-caking.
52	H_3PO_4 on kieselguhr: 82% of 90% acid	1·45	Various	20–85	Soft.
53	H_3PO_4 on kieselguhr: 65% of 100% acid	0·57	250° C. 3 hr.	—	Fairly hard cake.
54	H_3PO_4 on kieselguhr: 72% of 90% acid	0·704	250° C. 7 hr.	16	„ „ „
59	H_3PO_4 on silica gel: 48·5%	0·288	250° C. 6 hr.	43	Hard, form of original gel.
60	P_2O_5 on kieselguhr: 67/33	0·87	—	87·5	Moist, hygroscopic powder.
56	H_3PO_4 on kieselguhr: (repeated impregnations)	—	250° C. 48 hr.	*ca.* 30	Soft.
61	H_3PO_4 on kieselguhr: previously roasted to 900° C. for 4–5 hr. 82/18	1·45	250° C. 141·5 hr.	47	Hard white mass.
55	H_3PO_4 on kieselguhr: 82% of 100% acid	—	240° C. 167·5 hr.	30	Soft, hygroscopic.
62	75% of H_3PO_4 (90%)–10% $ZnCl_2$–15% kieselguhr	—	250° C. 42·5 hr.	30	Soft.
58	Meta phosphoric acid on kieselguhr 85/15	4·3	350° C. 77 hr.	25	Very hard.
63	H_3PO_4 on precipitated silica 72·5/27·5	—	240° C. 44 hr.	32	Fairly soft.
64	H_3PO_4 on technical silica 56·5/43·5	—	240° C. 92 hr.	32·5	Soft mass.
57	100% H_3PO_4 on roasted kieselguhr 82/18. Kieselguhr previously roasted 1000° C. 24 hr.	—	240° C. 167·5 hr.	37	Harder than No. 55.

TABLE XXI.

Results of Tests on Kieselguhr and Silica–Phosphoric Acid Catalysts (Exit gas rate 10 litres/hour in all tests.)

Cat. no.	Run no.	Temp. ° C.	Press. Lb./sq. in.	% Steam in inlet gas. Vol.	Duration. Hr.	Product. c.c.	Product catalyst weight ratio.	Product. Grm./100 g. cat. Hr.	Free acid content of cat. %. Initial.	Free acid content of cat. %. Final.	Total H_3PO_4 content of cat. Wt. Initial.	Total H_3PO_4 content of cat. Wt. Final.	Comments.
50	7	230	90–100	nil	75	786·5	10·5	14	8–11	1	69	64	
	10	230	120–130	½	85	853	10·2	12·0	—	—	—	—	
	23	230	150–130	7	163	1,028·5	14·6	8·95	1·0	1·9	73	70	Catalyst recovered in clean condition.
	26	230	140	5	61	697	8·5	13·8	43	2·5	70	—	
	28	230	130–100	nil	39·5	67·5	1·0	2·56	63	52	67	—	
52	3	230	130–115	½	167	2,735	31	18·6	47·5	28	—	66	Used catalyst black and sticky.
	13	230	170–150	5	87	1,724	18·9	21·7	82·85	26	86	—	
	20	230	170–120	nil	259	3,764	37	14·4	85	25	85	—	Catalyst in fairly good condition—a little carbonaceous material.
	21	230	170–130	,,	259	3,755	38·2	14·7	85	22	—	—	
59	18	230	120	,,	16	234	2·3	1·44	43	0·6	44	44	
	24	230	110	,,	15	16	0·15	1·0	—	—	—	—	
56	37	230	120–90	,,	66	1,635	6·3	9·6	32	18	86	—	Used catalyst—wet tarry mass.
	39	230	130–110	,,	94	1,978	23·2	24·7	32	22	86	—	
	42	200	130–80	,,	29	816	7·56	26	82	18	86	—	Pressure failure caused shut down. Catalyst hard and clean.
	43	230	130–80	,,	31·5	1,491	13·2	41·7	82	26	86	—	
	44	200	115–88	,,	77	1,251	11·4	14·7	32	22·5	86	—	Used catalyst—wet tarry mass.
	45	230	120–88	,,	77	2,300	30·8	42·8	32	12·9	86	—	
	46	230	130–100	7½	376	6,585	70·6	18·8	26	15·8	65·3	—	Used catalyst in reasonable condition. Run shut down due to choke.
	47	200	120–98	nil	137	909	9·2	6·75	26	15·5	65·3	—	
	48	230	122–110	,,	36	1,163	11·2	24·3	26	14·2	65·3	—	
	49	230	130–110	7·5	330	4,960	47·7	14·5	26	16·3	65·3	—	
	53	220	120–70	nil	254·5	2,339	26·7	9·83	22	16·7	71	72·5	Used catalyst very dirty and oily, but of good strength.
	54	230	120–80	,,	240	1,779	17·3	7·24	22	19	71	65?	
	100	230	90–140	16–10	331	10,395	104	31·4	9·6	16·5	64·5	64·3	This catalyst was previously used in Runs 44 and 54 and regenerated. See Text.
	118	280	100	20	90	2,310	18·2	20·3	22	17	82·4	82·4	Used catalyst mainly soft.
	202	230	150	7	89	3,165	25·6	28·6	30	—	92·5	—	Used catalyst in poor condition—choked.
61	90	230	85–100	nil	142	2,477	21·2	14·9	47	25·9	84·5	—	Used catalyst in very bad condition. Much gum.
	94	230	100–90	19	182	2,526	25·3	13·9	47	—	84·5	—	Catalyst in poor condition.
55	63	230	110	7	65	1,732	17·8	27·4	85·88	—	87	—	Shut down due to a leak.
	70	230	100	9	204	4,257	36·3	17·8	85·88	38·5	87	84	Used catalyst very dirty and oily.
	73	230	80–120	12	470	9,889	106	22·6	85·88	23	87	—	Used catalyst in a very bad condition.
58	62	230	100	nil	10	nil	nil	nil	2·2	2·3	45·2	—	Catalyst quite inactive.
	130	230	120	20	36	nil	nil	nil	25	31·8	55·7	—	Used catalyst—pasty mass—inactive.
	131	230	120	nil	19	3	0·02	—	25	29·2	55·7	—	,, ,, ,,

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heated at 250° C. for 6 hours. The resulting catalyst was of good appearance and hard, the catalyst retaining the original granular form of the silica gel. The free acid content was 43 per cent., but, as shown later, the catalyst was inactive because it contained no acid in excess of that which combined chemically with the silica gel. However, in the tests on this catalyst no steam was present in the inlet gas.

Mixtures of pure precipitated silica and technical silica with phosphoric acid gave soft catalysts, rather worse than those prepared from kieselguhr.

Details of kieselguhr and silica–phosphoric acid catalysts prepared are detailed in Table XX.

Results of Tests on Kieselguhr Catalysts. These are detailed in Table XXI, and show that catalyst deterioration in use is a feature of all such catalysts when no steam is added to the inlet gas. On the other hand, such deterioration is prevented by steam admixture. The variable results of Table XXI are due to the different drying treatments given to the catalysts before use. No. 58 catalyst, made up with meta-acid, is quite inactive, even when steam is present in the inlet gas—see Runs 62, 130 and 131.

Run 100 is of particular interest. The catalyst used was that previously employed in Runs 44 and 54 (at 230° C. but in the absence of steam), and treated with nitrogen at 300° C. for 48 hours to remove high-boiling but volatile polymers. The catalyst after treatment in this way was very much harder than it was before use in Runs 44 and 54, and was black in colour—very similar in appearance to gas coke, and of 9·6 per cent. free acid content. The very good result obtained in Run 100 shows that flushing with nitrogen at 300° C. is an effective means of regeneration—as is the case with other catalysts. After use in Run 100, the kieselghur catalyst was black and hard.

Alumina–phosphoric Acid Catalysts.

Alumina–phosphoric acid catalysts are considerably harder than the corresponding magnesia or kieselguhr catalysts of the same free acid content; but, because of the tri-valency of aluminium, have a lower free acid content for a given total H_3PO_4 content. The addition of copper oxide considerably increases the catalytic activity of alumina–phosphoric acid mixtures without decreasing the hardness.

Table XXII.

Cat. no.	Composition. Mole ratio $\frac{P_2O_5}{Al_2O_3}$.	Time and temperature of drying.	Total H_3PO_4 content.	Free acid content (%).	Appearance.
65	0·88	250° C. 1 hr.	62·7	23·0	Fairly hard.
		240° C. 22 hr.	62·7	trace	Vary hard.
66	0·48	250° C. 1 hr.	47·5	trace	,, ,,
67	1·07	240° C. 22·5 hr.	67·2	1·1	Rock hard.
68	4·0	240° C. 73 hr.	—	2·0	Fairly hard.
69	3·0	250° C. 23·5 hr.	85·0	5·4	Hard.
70	2·0	240° C. 19 hr.	80·0	2·8	,,
71	(Al_2O_3 : CuO : P_2O_5 = 1 : 1 : 2)	300° C. 21·5 hr.	68·2	1·8	Rock hard.

TABLE XXIII.

Tests on Alumina–Phosphoric Acid and Alumina–Copper Oxide–Phosphoric Acid Catalysts.

Cat. no.	Run no.	Temp. °C.	Pressure (lb./sq.in.)	% steam in inlet feed. Vol.	Product. c.c.	Product catalyst weight ratio.	Product. Grm./100 g. cat. Hr.	Duration of run. Hr.	% Free acid in used cat.	Comments.
67	91	230	120–105	nil	8	0·07	0·39	17	1·6	Used catalyst dry and hard.
67	127	230	125	21	6	0·049	0·3	16	3·2	Used catalyst hard, but damp.
69	126	230	150	20	551	4·6	4·5	102	19·0	Used catalyst brown, hard and dry.
69	133	230	150	nil	3	0·8	0·8	3	—	Catalyst became wet, plastic mass.
70	125	230	150	20	316	2·96	3·0	97	—	Used catalyst dry; good condition.
70	134	230	150	nil	30	7·5	2·8	3	—	Catalyst became wet, plastic mass.
71	105	230	80–110	nil	240	1·75	3·18	65	3·2	Used catalyst dry; good condition.
71	136	230	150	17	105	0·79	2·8	28	8·4	Used catalyst very hard.
71	137	230	105–95	nil	498	3·58	3·8	94	1·0	,, ,,
67	138	280	115–105	22	23	0·19	1·1	17	5·1	,, ,,
67	139	280	120–105	nil	7	0·054	0·3	18	trace	,, ,,

The catalysts in Table XXII have been prepared by calcining mixtures of alumina and 90 per cent. phosphoric acid.

Of the above catalysts, only Nos. 71 and 69 are of sufficient catalytic activity to merit attention, as shown in Table XXIII. Of these No. 71 is much the harder.

Nearly all alumina–phosphoric acid catalysts powder when left exposed to the air.

Other Phosphate Catalysts.

In addition to the catalysts described above, detailed tests have also been made on catalysts obtained by drying mixtures of phosphoric acid with the following:—Magnesia, floridin, supercell bauxite, firebrick, kaolin, pumice, various cements, spent shale, etc.

Of these, mixtures of acid with supercell, pumice or spent shale are satisfactory, the latter two being very hard and rugged. In addition, detailed tests have been made on the following phosphates, both neutral and acidic: zinc, boron, titanium, barium, calcium, tin, cerium, lead, strontium, iron, cobalt, nickel, chromium and manganese. A large variety of mixed phosphates have also been examined.

The choice of a phosphate catalyst for commercial use is governed by

(*a*) Cost.
(*b*) Activity.
(*c*) Initial ruggedness.
(*d*) Retention of mechanical strength during use.

With regard to cost of the catalyst, the initial cost is of minor importance, providing the catalyst is sufficiently rugged to withstand satisfactorily for long periods the conditions of reaction and regeneration.

Non-Phosphate Catalysts.

Numerous non-phosphate catalysts have also been examined during this investigation because of the undesirable volatile and corrosive properties of phosphoric acid. A satisfactory substitute for phosphoric acid has not been discovered, although tungstic acid and silico tungstic acid possess some activity.

Tungstic Acid, Tungstates and Silico Tungstic Acid. Tungstic acid has been used previously as a catalyst for the hydration of olefines to the corresponding alcohols in the presence of water vapour, and is mentioned in the following patents:—E.P. 335,551; E.P.392,685 and U.S.P. 1,873,536.

The use of tungstic acid as a catalyst in the vapour phase hydration of ethylene to ethyl alcohol is also described in a paper by Sanders and Dodge.[15]

With regard to polymerization, as far as is known, tungstic acid has not been suggested as a suitable catalyst, although in E.P. 415,792 is claimed the polymerization of ethylene in contact with a mixture of hydrocarbons rich in naphthenes in contact with a catalyst comprising an oxide of a heavy metal. Molybdenum oxide is specifically claimed for this reaction, and no mention is made of tungstic acid.

Tungstic acid was examined in the present programme in the pelleted condition (No. 72).

Tests were made at varying temperatures at 130–85 lb. pressure and a constant exit gas rate of 10 litres/hour (catalyst charge = 100 mls.), and the results in Table XXIV were obtained.

TABLE XXIV.

Run no.	Temp. ° C.	Press. Lb./sq. in.	Duration. Hr.	Product. C.c.	Product / Cat.	Product. Grm./hr./ 100 g. cat.
27	230	100–120	39	159	0·6	1·51
36	250	130– 95	75	295	1·14	1·52
40	250	110– 96	39	228	0·8	2·05
99	230	100– 85	39	111	0·37	0·96

In each case, after use, the catalyst was quite clean, but black, showing that reduction to lower oxides had occurred. In this connection it should be noted that gases such as propylene and butylene have a reducing action similar to that of hydrogen.

A test was made with tungstic acid previously reduced with hydrogen at 400–450° C. for 4 hours. In this case only 17 c.c. of product was produced in 11 hours over the temperature range 200–350° C., thus supporting the contention that reduction to lower oxides is responsible for the catalyst deterioration—probably reduction to the pentoxide (W_2O_5).

Experiments on re-oxidation of used tungstic oxide catalysts showed, however, that such catalysts can be effectively converted back to the trioxide condition by blowing with air at 400° C. for 20 hours.

Tests on pelleted ammonium tungstate to determine whether freshly prepared tungstic oxide was more effective were abortive. At 200–350° C. only 13 c.c. of product were obtained in 15 hours. When a small amount of steam was mixed with the inlet gas before passing over the catalyst, the yield of product obtained from tungstic oxide was not increased at 230° C.

Evidence that some decomposition to the trioxide had occurred was obtained by the evolution of ammonia during the warming-up period prior to the run.

Tests were also made on the following pelleted mixtures :—

No. 73. $WO_3 : ZnO = 1 : 1$ mole ratio.
No. 74. $WO_3 : MoO_3 = 1 : 1$ mole ratio.

but both these were ineffective.

The following catalysts were also examined :—

75	Aluminium tungstate—pelleted		
76	Cobalt tungstate	,,	
77	Cobalt tungstate	,,	(freshly prepared)
78	Phospho-tungstic acid	,,	
79	Silico tungstic acid	,,	

and the results in Table XXV obtained :—

TABLE XXV.

Cat. no.	Run no.	Temp. ° C.	Press. Lb./sq. in.	Duration. Hr.	Product. C.c.	Product / Cat.	Product. Grm./hr./ 100 g. cat.
76	102	230	90– 75	18	15	0·07	0·39
76	104	300	80– 90	14·5	7	0·06	0·41
78	87	230	80–110 – 88	42	79	0·23	0·56
75	109	230	110– 95	16	25	0·14	0·9
79	151	230	—	108	561	1·97	1·82
77	156	230	150	37	51·5	0·23	0·62

Other Metal Oxides. Tests have also been made on the following oxides at 150 lb. pressure and 200–350 per cent., but none of these possesses sufficient activity to be attractive commercially :—

Molybdic oxide	MoO_3
Uranium trioxide	WO_3
Vanadium pentoxide	V_2O_5
Titania	TiO_2
Chromium oxides	CrO_3 and Cr_2O_3

Alumina on silica gel is slightly active and does not deteriorate rapidly in use. Alumina and silica gels are similar in these respects.

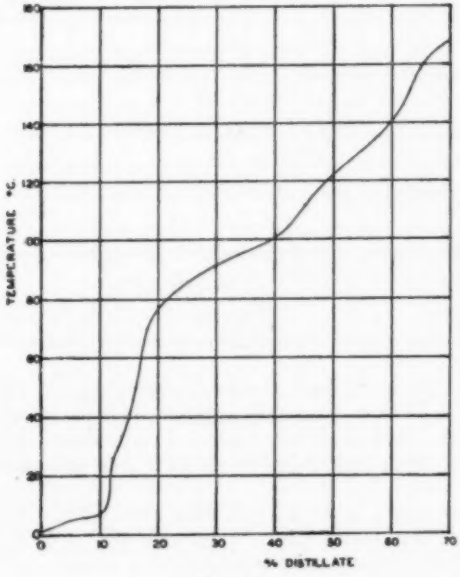

FIG. 19.

TRUE BOILING POINT CURVE POLYMER PRODUCT.

Materials such as acid sulphates and cuprous chloride are also slightly active catalytically.

Properties of Products Obtained by Catalytic Polymerization of Olefines.

All phosphoric acid or phosphate catalysts, operating at the same temperature give essentially the same product; the spirit fractions are also of the same octane number (*i.e.* 78–82 C.F.R. Motor Method). It should be noted, however, that the spirits examined are not stabilized, and

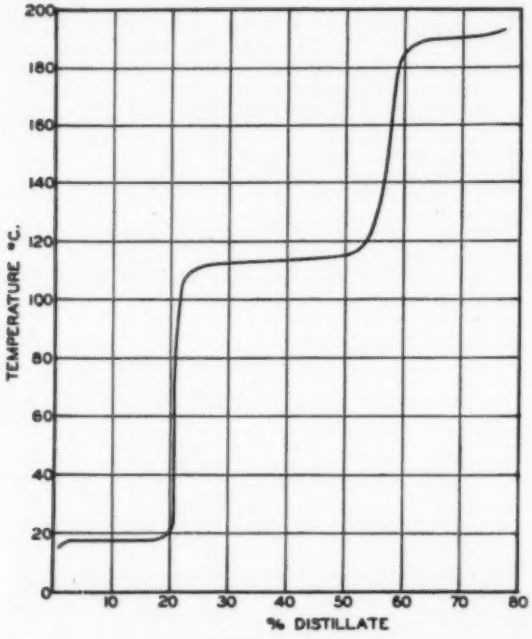

Fig. 20.

TRUE BOILING POINT CURVE POLYMER PRODUCT FROM CRACKED C_4 FRACTION.

do not include light ends carried away in the exit gas. The true boiling-point curve of a product from acid cadmium phosphate catalyst is reproduced in Fig. 19. This is entirely typical of all products obtained from the stabilizer reflux feed, and shows no decided flats corresponding to pure compounds.

On the other hand, catalytic polymers obtained by the treatment of cracked C_4 fractions under mild conditions (150 ° C.) consist mainly of dibutenes and tri-butenes—as shown in Fig. 20.

The anti-knock blending value of catalytic polymer spirit is of particular importance. In Figs. 21–23 are plotted the C.F.R. Motor Method octane numbers of this material in three different base spirits. The blending value,

expressed in terms of "blending octane numbers" * is naturally greatest in base spirits of low octane ratings, and Fig. 24 shows how the blending octane number ranges from 115 to 82 according to the nature of the base spirit.

The octane numbers of fractions of catalytic polymer spirits show little

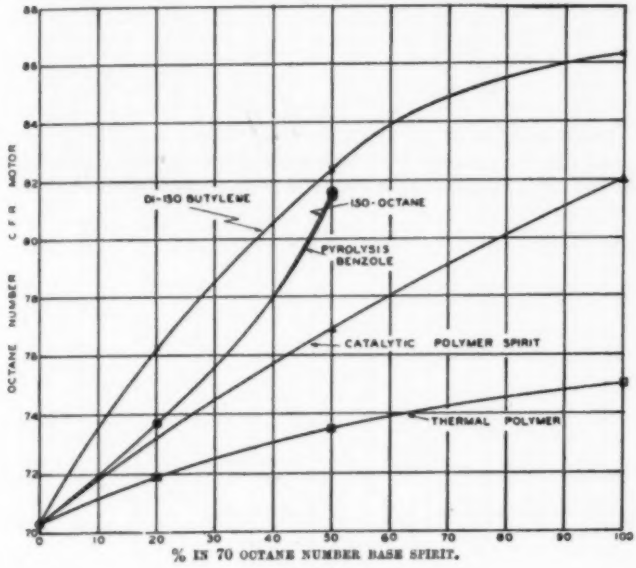

FIG. 21.

OCTANE NUMBERS, BLENDS OF SYNTHETIC FUELS.

variation with boiling point, as shown in the following figures referring to material produced from reflux liquid using granular acid cadmium phosphate catalyst :—

Fraction b. pt. (° C.).	Neat.	C.F.R. Motor Method octane numbers 30 per cent. in 52·5 octane no. base spirit.	70 per cent. in 52·5 octane no. base spirit.
25– 50	—	70·4	89·6
50– 75	83·2	69·8	78·7
75–100	81·9	71·2	79·3
100–125	81·9	72·2	78·9
125–150	80·8	72·2	78·5
150–175	82·3	70·5	79
175–200	80·6	69·6	78·4
200–225	80·2	68·2	78·5

* The "Blending octane number" of a spirit is calculated as follows :—

Octane number of blend = Octane number of base × Concentration + Blending octane number of added spirit × Concentration.

E.g. if a 50/50 blend of base spirit and a polymer spirit has an octane number of 74 and the base spirit alone has an octane number of 52·5, then the "Blending octane number" of the polymer spirit at this concentration is given by :

$$74 = 52{\cdot}5 \times 0{\cdot}5 + \text{Blending octane number} \times 0{\cdot}5$$

$$\therefore \text{Blending octane number} = \frac{74 - 26{\cdot}25}{0{\cdot}5} = 95{\cdot}5.$$

On a further sample of the same material the following figures were obtained :—

Fraction b. pt. (° C.).	Neat C.F.R. Motor Method octane numbers.
0– 96	82·5
96–107	82·3
107–119	82·1
119–167	81·4
167–187	80·8
187–209	80·7

The octane number of the spirit produced from a cracked C_4 fraction is 78–82, and does not change from this value if the *iso*butene content of the feed (25 per cent. by volume) is removed prior to catalytic polymerization.

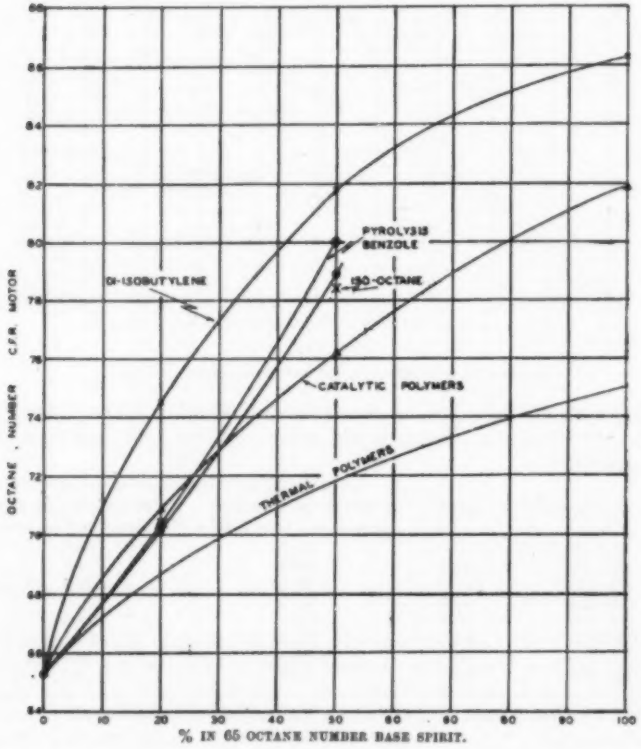

FIG. 22.

OCTANE NUMBERS, BLENDS OF SYNTHETIC FUELS.

Details of the properties of typical polymer products are given in Table XXVI.

TABLE XXVI.

Details of Properties of Typical Polymer Products Obtained by the Use of Phosphate Catalysts.

Feed.	Stabilizer overhead.	Cracked C_4 fraction.
Crude Product:—		
Sp. gr.	0·750	0·750
Aniline point (° C.)	39	40
Percentage at 140° C.	56	41·5
Percentage at 200° C.	82	83
Spirit Fraction:—		
Sp. gr. at 60° F.	0·750	0·740
Initial b.pt. (° C.)	44	27·5
10 per cent. distillate at	84	81·5
20 " " "	96	111
30 " " "	102	120
40 " " "	115	125
50 " " "	125	130
60 " " "	136	144
70 " " "	154	172
80 " " "	168	185
90 " " "	181	192·5
Final b.pt.	198	197
Percentage loss	2	4
Percentage at 100° C.	20	13
Aniline point (%)	38	41
Octane number (C.F.R. motor method)	80–82	82
Residue Fractions:—		
Sp. gr. at 60° F.	0·858	0·872
Initial b.pt. (° C.)	215	222
10 per cent. distillate at	229	235
20 " " "	234	240·5
30 " " "	239	245·5
40 " " "	243	250
50 " " "	251	255
60 " " "	260	262
70 " " "	277	270
80 " " "	305	286
90 " " "	—	314
Final b.pt.	348	320
Percentage at 300° C.	78	86
Total distillate (%)	98	99
Aniline point	47	53·8

The Refining of Catalytic Polymers.

The conclusions arrived at in refining tests on catalytic polymer spirits may be summarized as follows, all the work being done on polymers produced from desulphurized stabilizer overhead feedstock.

1. 200° E.P. distillates from the crude polymer are practically water white, but very unstable to normal gum tests. A finished spirit of specification gum content and gum stability has not been produced by the normal acid treatment applied to the total polymer. The potential gum content of the polymer spirit increases rapidly with boiling point.

2. 200° E.P. distillate from crude polymer spirit may be stabilized against gum formation to an extent satisfactory for normal conditions by the addition of inhibitors.

3. A 15–85 mixture of crude polymer with normal cracked spirit can be refined to give a finished product of good colour and gum stability by conventional acid treatment followed by redistillation and final neutralization. The amount of acid required is very small.

Alternatively, the crude polymer may be fed to the cracking plant primary tower as reflux—in which case the polymer bottoms pass to cracking stock and the polymer spirit is blended with cracked distillate for refining. The polymer bottoms crack readily to give a spirit of 80 octane.

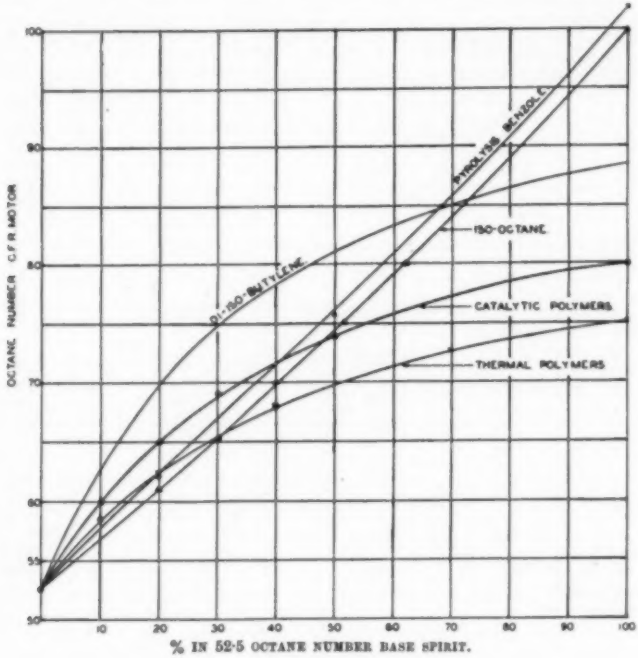

FIG. 23.

OCTANE NUMBERS OF SYNTHETIC FUELS. (C.F.R. MOTOR METHOD.)

Catalytic polymer bottoms (*i.e.* the fraction boiling above 200° C.) is at the moment of little use as a diesel fuel, the cetene number being only about 35, and is obviously better employed as a depolymerization stock.

REDUCTION OF POLYMER SPIRITS.

The reduction of catalytic polymers to give saturated paraffinic materials is of considerable importance in view of the possible production of materials similar to *iso*octane—which is obtained by the reduction of di*iso*butylene.

1. Polymer spirit produced from cracked butylene feed, containing up to 20 per cent. *iso*butylene, is considerably improved by catalytic

reduction—the octane number increasing from 80–82 to 95–100. The reduced spirit is absolutely gum stable, and constitutes an aviation fuel component of excellent quality.

2. Polymer spirit produced from cracked butylene feed, from which the *iso*butene content had previously been removed, was reduced in the presence of a suitable catalyst at 200–240° C. and super-

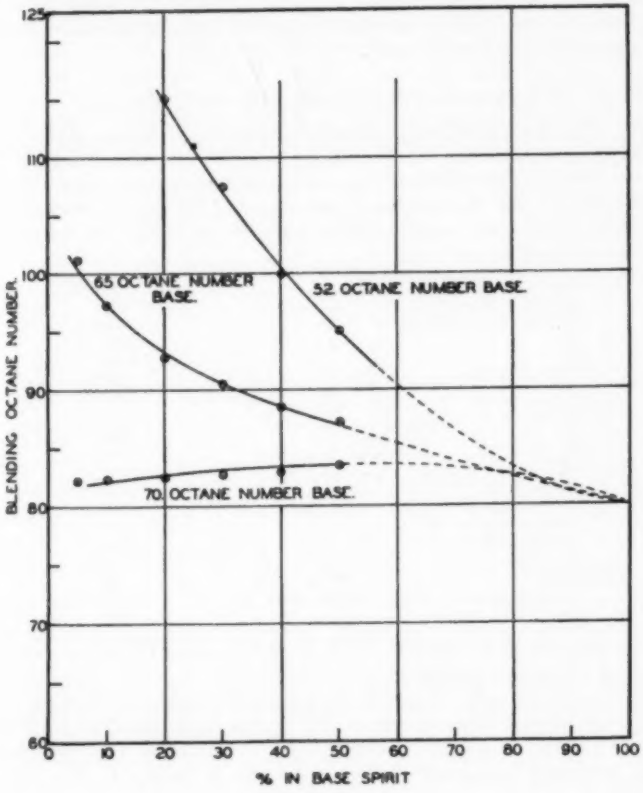

FIG. 24.

BLENDING OCTANE NUMBERS OF CATALYTIC POLYMERS IN VARIOUS BASE SPIRITS.

atmospheric pressure. By this treatment the neat octane number (C.F.R. Motor Method) fell from 80·7 to 74·5.

3. Polymer spirit produced from stabilizer C_3–C_4 overhead (containing 8–10 per cent. *iso*butylene) at 150–200° C. was reduced and the octane number remained substantially constant (initial value 80·8: final value 80·4). The octane numbers of corresponding blends in base spirits fell considerably after reduction.

4. No appreciable improvement in octane rating can be achieved

by hydrogen reduction of *fractions* from polymer spirit obtained by polymerization of feed stocks containing both C_3 and C_4 olefines. The "di*iso*butylene" fraction present in such polymers is very small and its isolation is definitely uneconomic.

It is evident that the only reasonable method of producing dibutenes by catalytic polymerization capable of being reduced to 100 octane material is to treat a C_4 fraction rather than a C_2–C_3–C_4 mixture. In the latter case the C_4 components condense with both C_2 and C_3 hydrocarbons and the yield of dibutenes is therefore reduced.

The Catalytic Polymerization of Ethylene.

Tests using acid cadmium phosphate catalyst have shown that ethylene will polymerize, although the conditions required are more drastic than in the case of the higher olefines. In autoclave experiments using this catalyst at 350° C., 900 lb. maximum pressure and 270 mins. reaction time, the product produced contained 57·5 per cent. by weight of spirit of the following properties :—

Sp. gr. at 60° F.	0·734
Initial b. pt. (° C.)	37
10 per cent. distillate at	70·5
20 " " "	85
30 " " "	100
40 " " "	114·5
50 " " "	129
60 " " "	143
70 " " "	156
80 " " "	170
90 " " "	186
Final b. pt. (° C.)	205
Percentage at 100° C.	30
Percentage at 140° C.	58
Total distillate	97·5
Residue	1·5
Loss	1
Octane number (C.F.R. Motor Method)	76
Bromine number	93

In the absence of a catalyst, ethylene yields, under the same conditions, a spirit of 73 octane number.

Ethylene can be polymerized in the presence of acid cadmium phosphate catalysts at temperatures as low as 300° C., the spirit obtained at this temperature having an octane number of 78·5. At higher temperatures the spirits produced had lower octane numbers, as shown in the following figures :—

Temperature of Polymer (° C.).	Octane number of Spirit (C.F.R. Motor Method).
300	78·5
325	77·2
350	76–74·3

This observation is in line with the fact that at the higher reaction temperatures the primary polymerization products undergo isomerization to give a complex mixture of olefines, paraffins, naphthenes and aromatics.

A further effect of increase in reaction temperature is to increase the amount of 200° E.P. spirit present in the product. At 350° C. the product contains 66 per cent. spirit and at 300° C., 57 per cent.

Design Data for Large-scale Catalytic Polymerization Plants.

The equipment required for large-scale catalytic polymerization plants is very simple and, because the reaction conditions are very mild, comprises only normal refinery plant.

A typical flow diagram is given in Fig. 25 in its simplest form. The process can be operated at 150–300 lb./sq. in., and can thus operate at the pressure at which stabilizer overhead or absorber residue gases are available. This eliminates feed pumps and compressors. The temperature required in the reactors is generally 250° C. maximum, and hence the preheat furnace required need only contain convection banks. The requisite amount of steam is injected into the gas before or after the preheat furnace. In the flow diagram shown the gas flows through the reactors in parallel, but

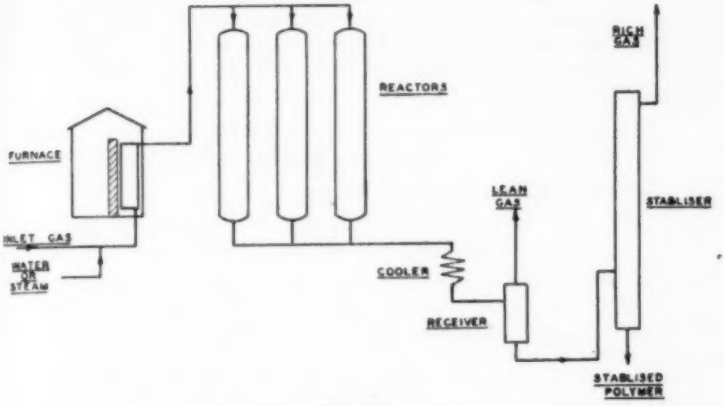

Fig. 25.

TYPICAL FLOW DIAGRAM LARGE-SCALE CATALYTIC POLYMERIZATION PLANT.

valves and by-pass lines are required to enable parallel or series operation to be chosen at will and to allow the gas to pass through the reactors in any order. It is also necessary to arrange these valves so that any reactor may be on regeneration while the others are on stream.

After passage through the reactors, the gas is cooled and the product stabilized in conventional equipment after the liberation of lean gas in a receiver. Recycle material may be taken from the stabilizer top, and if the reflux pump on the stabilizer is of sufficient capacity to return recycle to the preheat furnace, no additional recycle pumps are required.

The only factor of importance in the design of such equipment is the dissipation of heat from the reactors. As already mentioned, the exothermic heat of reaction is approximately 440 B.Th.U. per lb. of olefines polymerized. In the case of a gas rich in olefines this is much more than the amount of heat required to preheat the inlet gas to reaction temperature, and must be dissipated. The method in favour for temperature control in the reactors is the injection of cold recycle material into the catalyst at

various points. For efficient control this recycle material should, of course, be low in olefine content.

With reference to design figures, it is possible to obtain at least 90 per cent. conversion of olefines to total polymers in continuous operation with an active catalyst at an inlet gas rate of 3–5 cu. ft. per lb. of catalyst per hour, measured at N.T.P.

An average figure for the 200° E.P. spirit content of the crude polymers is 85 per cent. by volume. Steam injection should be in amount equivalent to 2–10 per cent. by volume of the inlet gas (measured at N.T.P.).

Sulphuric Acid Polymerization.

A further very satisfactory method of polymerization involves the use of sulphuric acid. The method is at present restricted to the polymerization of *iso*butylene and acid of 55–76 per cent. concentration is employed. The process is operated very simply by contacting butane fractions containing *iso*butylene with sulphuric acid of this strength and then subjecting the mixture obtained to a temperature of 60–120° C. The reaction occurs in two distinct steps.

1. Hydration of *iso*butylene to *tert.*-butyl alcohol

$$C_4H_8 \longrightarrow C_4H_9{\cdot}OH$$

2. Dehydration and polymerization

$$2C_4H_9{\cdot}OH \longrightarrow (C_4H_8)_2 + 2H_2O$$
$$3C_4H_9{\cdot}OH \longrightarrow (C_4H_8)_3 + 3H_2O$$

The polymers produced in the second stage of the reaction consist of a mixture of di- and tri-*iso*butylenes boiling over the range 100–185° C. and require only a small alkali wash to give a material of pleasant odour and octane number (C.F.R. motor) of 85–90.

The relative proportion in which di- and tri-*iso*butylenes are formed is determined by the concentration of the acid employed. Using 75 per cent. sulphuric acid at 50–60° C., the proportion of tri-*iso*butylene is high, and moreover polymers boiling outside the gasoline range are also produced. A further effect of using 75 per cent. acid is that the product obtained contains straight-chain compounds, formed from butadiene and normal butenes which on hydrogenation give paraffins of low octane number.

Using 55 per cent. acid, the two reactions given above occur separately, and hence can be individually controlled. In the first stage it is possible to build up considerable concentrations of tertiary butyl alcohol in the acid layer, and the second stage can be readily effected without isolating the alcohol merely by heating the acid layer to a temperature above about 65° C. In this way the water removed from the acid by formation of alcohol in the first stage is regenerated, so that on removal of the supernatant hydrocarbon layer there remains acid of the same concentration as that originally employed for the *iso*butylene absorption. Unlike the spent acid which remains after operating with 75 per cent. concentration at 50–60° C., this recovered acid is clean, light yellow in colour and may be used continuously without treatment. With acid of concentration below 50 per cent. the rate of absorption is very slow.

The polymers produced are of particular value in that they may easily

be converted into 100 octane number material (*iso*-octane and *iso*dodecane) by catalytic non-destructive hydrogenation (*i.e.* reduction).

Typical analyses of the products obtained in commercial plants are as follows :—

	Polymers. (Di-*iso*-butylene.)	Hydrogenated polymers. (*iso*Octane.)
Sp. gr. at 60° F.	0·7215	0·697
Initial b. pt.	62	80
2 per cent. distillate at	—	94
5 " " "	—	96·5
10 " " "	98	97·5
20 " " "	101	98·5
30 " " "	101·5	99
40 " " "	102	99·5
50 " " "	103	99·5
60 " " "	103·5	100
70 " " "	104·5	100·5
80 " " "	106·5	101
90 " " "	112·5	103·5
Final b. pt.	172	143
Bromine number	—	1·0
Gum (actual + potential), mg./100 ml.	1·0	below 1·0
Octane number (C.F.R. Motor Method)	87	99

The authors desire to express their thanks to the Chairman of the Anglo-Iranian Oil Company for permission to publish this paper.

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THE RHEOLOGICAL PROPERTIES OF ASPHALTIC BITUMENS.*

Dr. Ir. J. Ph. Pfeiffer and Ir. P. M. van Doormaal.

Introduction.

Asphaltic bitumens are employed in an almost unlimited number of technical applications. Besides road-making, there are numerous industrial applications, examples of which are: the roofing felt industry, the paper and textile industries, the cable industry, the manufacture of briquettes and of bitumen compositions for the protection of pipe-lines or for the production of bituminous paints, etc.; further, of late years they have come to be used for various hydraulic purposes as well. For this reason it has become necessary to acquire a thorough knowledge of the physical and chemical properties of these materials.

The necessity for understanding the factors governing the physical and chemical behaviour of the asphaltic bitumens forces itself upon the producers, not only with a view to the *sale* of the products, but also because suggestions have to be made as to the most efficient manufacturing process.

Although it is highly important to have a clear insight into the constitution of asphaltic bitumens, only little is, in general, known about this subject. This may be accounted for by the fact that asphaltic bitumens, being the evaporation or reaction residues of petroleum, which are extremely complicated mixtures of hydrocarbons, form a possibly even more intricate system of molecular types, to which comparatively few physical research methods are applicable, and which has hitherto practically defied all chemical methods of research.

The slight chemical reactivity of the asphaltic bitumens, which renders them particularly suitable for numerous technical applications, is at the same time responsible for the inefficiency of many chemical methods of analysis; on the other hand, the technical specifications for some properties have given a greater prominence to physical research methods. Therefore, the laboratory of the Bataafsche Petroleum Maatschappij at Amsterdam has started an extensive research in this direction, of which some results are given in the following pages.

The insight into the subject matter to be dealt with here has admittedly not yet assumed a universally adopted form. The authors do not, therefore, wish to have the hypotheses evolved looked upon as a completed study, but rather as more or less approximate working hypotheses which are liable to future modification and which may be of importance for the general information of those interested in the subject.

Classification of the Asphaltic Bitumens Based on Their Rheological Properties.

As in nearly all technical applications of asphaltic bitumens, the material has to be worked up at a comparatively high temperature, while, after

* Paper received 23 April, 1936.

cooling, the product is required to possess a definite "hardness," it is natural that physical laboratory research work has been especially directed towards problems relating to the viscosity and the changes of this property as a function of the temperature.

The wide temperature range over which viscosity determinations have to be made for the great variety of bitumen applications and the great divergence in hardness of the various grades make it necessary to measure viscosities ranging from 1 to 10^{10} poises. In consequence of these widely divergent magnitudes, the viscosities have to be determined by different methods.

Dr. R. N. J. Saal [1, 2] has given a survey of various methods of absolute viscosity determinations, reducing the results of the different conventional methods to values for the viscosity (η) in poises. As, in these examinations, a great number of asphaltic bitumens showed phenomena such as plasticity, elasticity and thixotropy, this conversion has only an approximative character in these cases.

For asphaltic bitumens behaving entirely, or practically entirely, as purely viscous liquids, the following relations were found :

(*a*) Based on penetration test

$$\eta = \frac{5{\cdot}13 \,.\, 10^9}{\text{pen.}^{1{\cdot}93}} \text{ poises}$$

(*b*) Viscosity at the melting point, Ring and Ball :

$$\eta = \text{about } 1{\cdot}2 \,.\, 10^4 \text{ poises.}$$

From these two formulæ it follows that the penetration at the Ring and Ball melting point amounts to about 800, a value which, as will be shown later, is confirmed, in order of magnitude, by experiment, also for asphaltic bitumens deviating from the purely viscous type.

For the practical utility of a classification system it is, however, necessary that this be based on routine determinations, as absolute viscosity measurements take up too much time.

For a great many technical applications the changes in consistency between 0° C. and the temperature of the melting point R. & B. form a highly important factor in judging the utility of an asphaltic bitumen. Since the consistency of the usual bitumen grades within this temperature range is generally indicated by the penetration and the temperature of the melting point R. & B., these tests now having been universally adopted in the analysis of bitumens, we have attempted to characterize asphaltic bitumens by the values found for the penetrations at different temperatures and for the melting point R. & B.

We have based our deductions on the consideration that, if the temperature is not too high (*e.g.* about 60° C.), the logarithm of the penetration is, generally, a linear function of the temperature, so that :

$$\log \text{pen.} = K_1 + \alpha t \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation α is characteristic of the temperature susceptibility; according as α is greater or smaller, the bitumen is called more or less sensitive to temperature change; K_1, representing the logarithm of the

penetration at 0° C., is defined by the hardness and, consequently, by the degree of distillation of the bitumen.

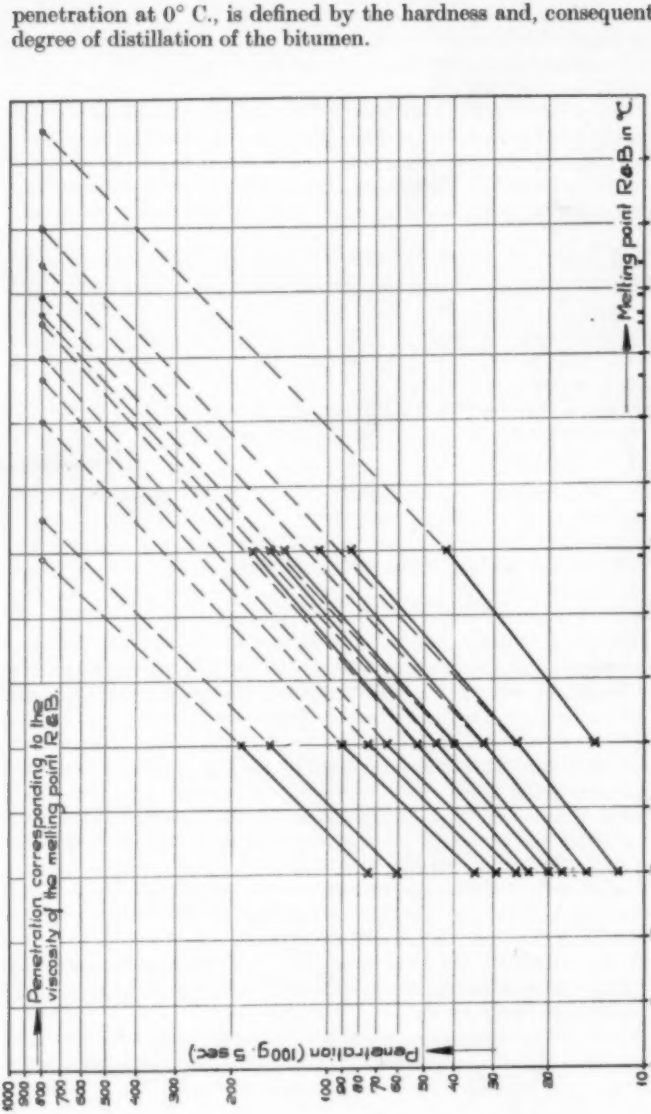

Penetration (100g, 5 sec)
Penetration corresponding to the viscosity of the melting point R&B.
Melting point R&B in °C
Penetration temp.

Fig. 1.
Penetration curves of Mexican Steam-refined bitumens. (made by steam distillation of the same base material.)

In Fig. 1 the penetration–temperature lines (= full lines) of a number of Mexican steam-refined bitumens are given.

From this graph it may be seen that the penetration–temperature lines of grades of different hardness, made by a simple steam distillation of the

same base material, show a weak convergence, in this sense that in the direction of the harder grades the angle α and, together with this, the susceptibility slightly decrease.

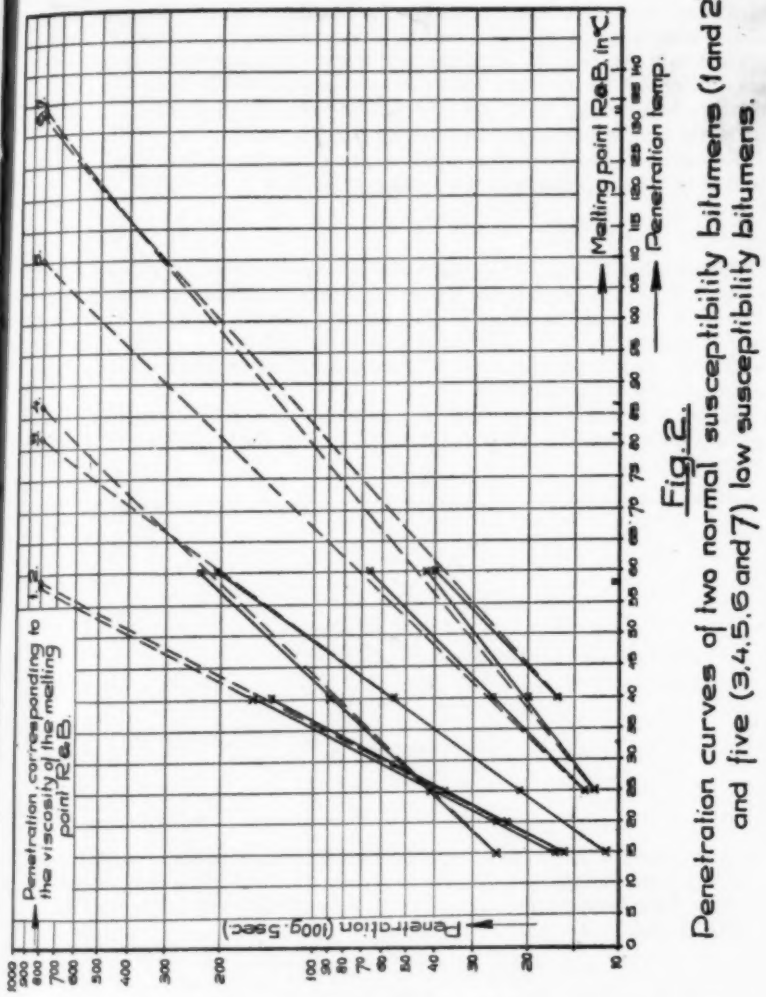

Melting point R&B. in °C
Penetration temp.
Penetration (100g. 5sec.)
Penetration corresponding to the viscosity of the melting point R&B.

Fig. 2.
Penetration curves of two normal susceptibility bitumens (1 and 2) and five (3, 4, 5, 6 and 7) low susceptibility bitumens.

In addition, the consistency of the various Mexican asphaltic bitumens at the temperature of the melting point R. & B. proves roughly to be expressed by a value for the penetration of 800. In other words, if in Fig. 1, where the penetration has been plotted against the temperature for the bitumens of different hardness, points are plotted with ordinate pen. = 800 and with

abscissa the temperature of the melting point R. & B., the points are approximately on a line with the values for the penetration determined at a lower temperature.

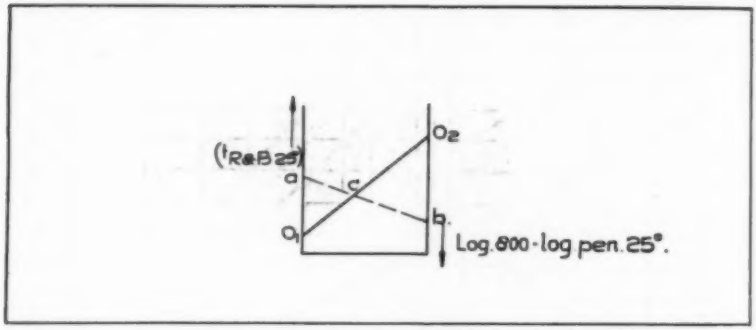
Fig. 2, which, besides a number of normal susceptibility bitumens, refers also to some very low susceptibility bitumens, shows that for these strongly blown bitumens too the temperature of the melting point R. & B. corresponds to a constant value of the penetration of approximately 800. It may therefore be assumed that for most asphaltic bitumens the linear relation between log pen. and temperature remains approximately valid up to the temperatures near the melting point R. & B.

Equation (1) must therefore apply at the pen. temperature of 25° C., as well as at the temperature of the melting point R. & B., so that [3]

$$\log 800 - \log \text{pen.}/25^\circ\text{ C.} = \alpha(t_{\text{R. \& B.}} - 25^\circ\text{ C.}) \quad . \quad . \quad (2)$$

Hence, when for all the bitumens of different hardness but with the same susceptibility α, a graph is made showing the relation between the penetration at 25° C. and the corresponding melting point R. & B., in which (log 800 — log pen./25° C.) is plotted on the ordinate and ($t_{\text{R. \& B.}} - 25^\circ$ C.) on the abscissa, a straight line is obtained, of which the slope α at once shows the susceptibility of the materials.

When (log 800 — log pen./25° C.) and ($t_{\text{R. \& B.}} - 25^\circ$ C.) are plotted in opposite directions on two parallel scales, at any given distance from each other, thus:



and the penetration (b) of a bitumen is connected with the corresponding melting point R. & B. (a), this line ab crosses the line O_1O_2 connecting the O points of the temperature and penetration scales in point c, the position of which is such that

$$\frac{O_2c}{O_1c} = \frac{O_2b}{O_1a} = \frac{\log 800 - \log \text{pen.}/25^\circ\text{ C.}}{t_{\text{R. \& B.}} - 25^\circ\text{ C.}} = \alpha.$$

The position of point c on the line O_1O_2, which is the same for all the bitumens of different hardness but the same susceptibility (since for these grades α is constant), is, therefore, characteristic for the temperature susceptibility of the penetration of the bitumen. In the accompanying

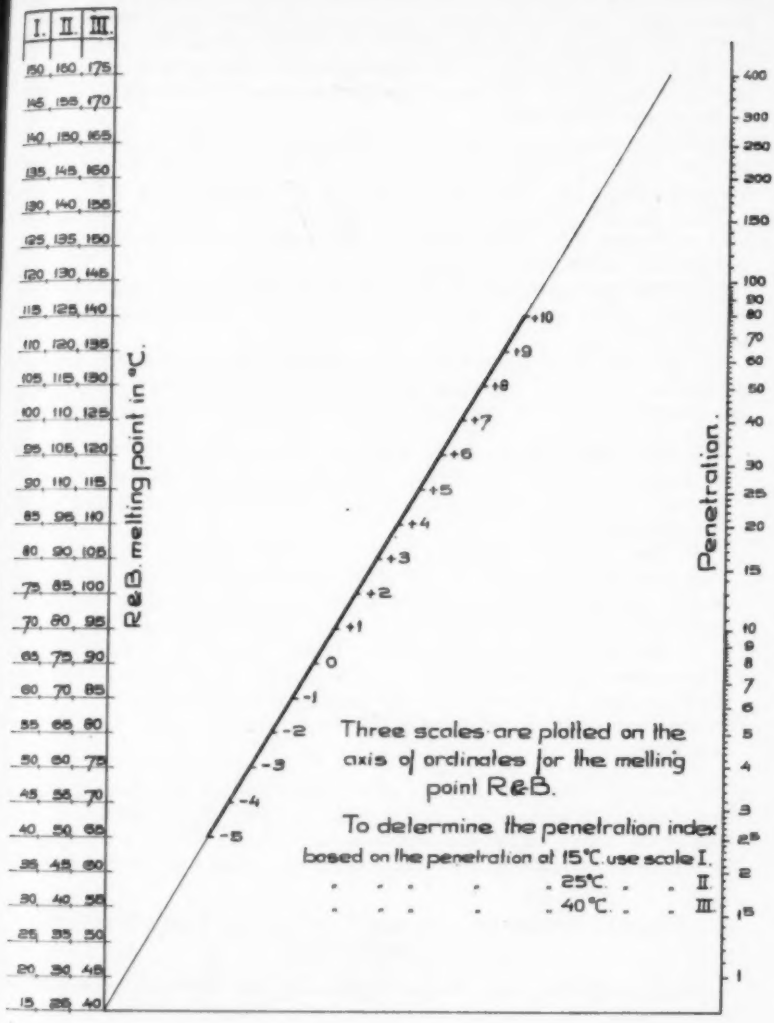


Fig. 3.

Diagram to determine the penetration index of asphaltic bitumens.

nomogram (Fig. 3) division marks have been placed on the line O_1O_2; the O point of this " index nomogram " corresponds to the temperature susceptibility of the, not too hard, steam-refined Mexican bitumens (*e.g.* $t_{R.\ \&\ B.}$ = 40° C., pen./25° C. = 200). The bitumens with a higher temperature susceptibility than those with index O have a negative, the lower-susceptibility bitumens a positive index.

With this nomogram a high-susceptibility bitumen with $t_{R.\ \&\ B.} = 38{\cdot}5°$ C. and pen./25° C. = 146 is found to have an index = − 2·0, a low-susceptibility bitumen with $t_{R.\ \&\ B.} = 85$ and pen./25° C. = 36, an index = + 4·2.

When the different degrees of susceptibility have once been indexed, the lines indicating a constant index (the iso-index lines) can be drawn in a penetration–melting point diagram (Fig. 4).

It follows from equation (II) that these lines converge towards the point with pen. = 800 and $t_{R.\ \&\ B.} = 25°$ C., while they are asymptotic to the melting point axis.

On the strength of the differences in temperature susceptibility the asphaltic bitumens can be grouped in three classes merging into one another, the boundaries of which have been chosen more or less arbitrarily.

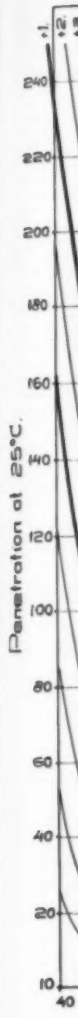
1. The class with an index between − 1 and + 1, the " *N type.*" This class comprises most steam-refined bitumens (such as the Mexican), generally used for road making; these are therefore sometimes called " normal bitumens."
2. The class with an index below − 1, the " *Z type.*" This class is also sometimes indicated by the name of coal tar pitch type. Like the coal-tar pitches, the bitumens of this type are characterized by their great susceptibility and, in general, also by their great brittleness.
3. The class with an index above + 1, the " *R type.*" In addition to a low-temperature susceptibility, these bitumens are generally characterized by slight brittleness. As the majority of the blown bitumens have these characteristics, this type of bitumen is also sometimes indicated as the blown type.

It should be observed that not all straight-run bitumens belong to the normal type, nor all blown bitumens to the R type. There are blown bitumens of the Z type and of the normal type, while, on the other hand, both the Z type and the R type are found among the straight-run bitumens.

General Hypotheses on the Rheological Properties of Asphaltic Bitumens.

Before continuing our theories concerning the viscosity of asphaltic bitumens, the nomenclature to be used when describing the rheological properties should first be discussed. Only recently Houwink [4] gave a survey of the various cases which may present themselves from a theoretical viewpoint.

This investigator argues that, if $\frac{dv}{dy}$ is the rate of shear, T the shearing stress, experience shows that in general the change of the $\frac{dv}{dy} - T$ function



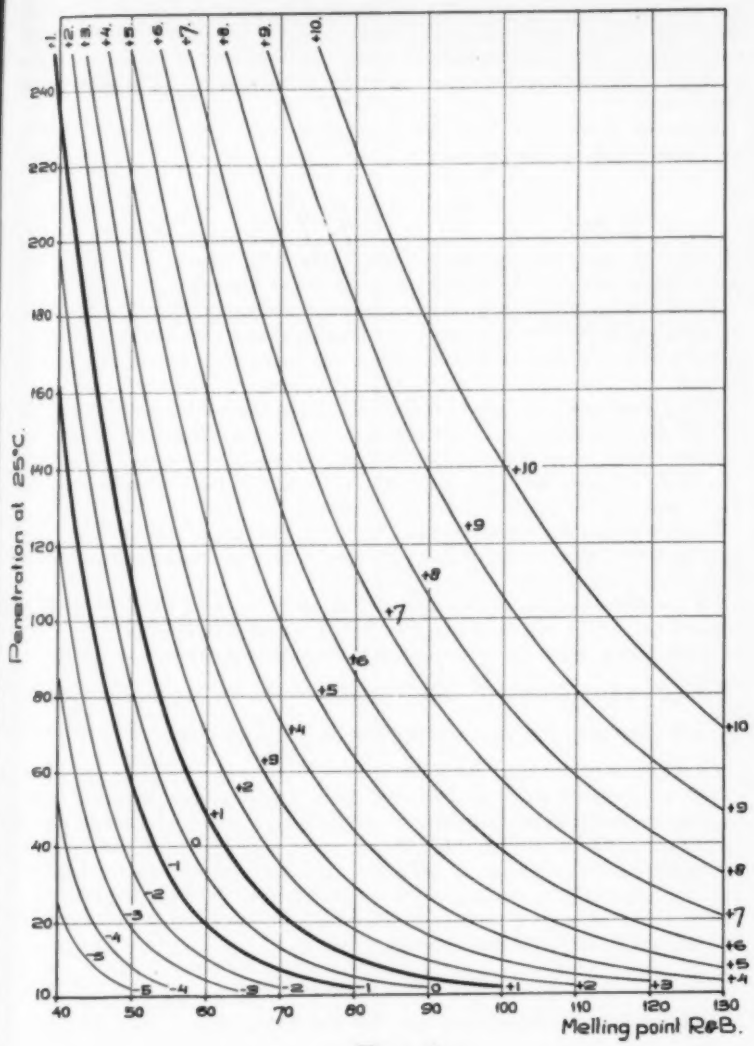


Fig. 4.

Classification of asph. bitumens in various types, based on the relation between. Penetration at 25°C and melting point R&B.

can be represented by a diagram of the type as given in Fig. 5*a*; further, that the rate of shear–shearing stress diagram is characteristic of the flow properties of the material in question and may form the basis for the analysis of deformation processes in so far as these are attributable to the flow.

Houwink points out that the changes in the $\frac{dv}{dy} - T$ curve can be expressed by the following formula:

$$\frac{dv}{dy} = \psi\,(T - f)n;$$

in four "shear–shearing stress" diagrams (Fig. 5*b*–5*e*) he shows the possibilities which can be derived from the above formula.

The flow phenomena illustrated by figures *d* and *e* refer to materials which, under the influence of a shearing stress smaller than a given value *f*, show no shear at all, hence to materials with a yield-value (*i.e.* a critical shearing stress).

It is not quite certain whether asphaltic bitumens have a yield value, nor is this easy to detect, as in the range of very low shearing stresses and corresponding low deformation rates it is practically impossible, in connection with the elasticity to ascertain in how far the deformations are attributable to flow or to elastic deformation.

In view of this there is little point, when examining asphaltic bitumens, in making a fundamental difference between the flow phenomena described in Fig. 5*d* and 5*c* and those of Fig. 5*b* and 5*c*.

Of the flow phenomena depicted in Fig. 5*b* the type of flow indicated by curve 4 has, so far, not been observed by us in asphaltic bitumens.

With regard to the flow phenomena represented by curves 2 and 3, it may be observed here that, if $\frac{dv}{dy} = \psi\, T^n$ is plotted, curves are obtained in the $\frac{dv}{dy} - T$ diagram with their convex side to the T axis if $n > 1$, and with their concave side to the T axis if $n < 1$.

Our co-operator R. N. J. Saal has never found values of $n < 1$ when making viscosity determinations on asphaltic bitumens; in other words, he invariably finds curves with their convex side to the T axis. These observations tally completely with the viscosity determinations made by Houwink on artificial resins, which also invariably gave convex curves to the T axis. It may therefore, in general, be assumed that the viscosity decreases with an increasing shearing stress.

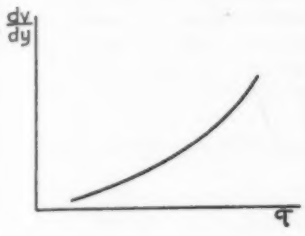
Nomenclature.

It follows from the above that for the description of the rheological properties of asphaltic bitumens it is practically sufficient to consider the flow phenomena represented by curve 1—which we shall call "*purely viscous flow*"—and those by curve 3, which we shall call "*plastic flow*."

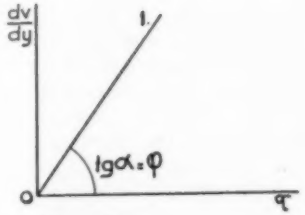
By accepting this nomenclature for the word "plastic," we adopt the definition given by Bingham.[5]

> "If in non-turbulent flow, the ratio of flow to force is constant, the material is said to be fluid; otherwise it is plastic."

a.



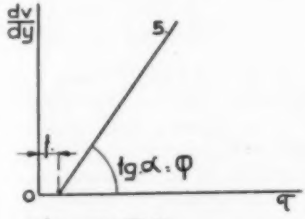
b.



$\frac{dv}{dy} = \varphi\tau$

φ = fluidity = $\frac{1}{\eta}$.

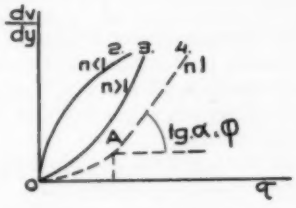
c.



$\frac{dv}{dy} = \varphi(\tau - f)$

φ = fluidity = $\frac{1}{\eta}$

d.



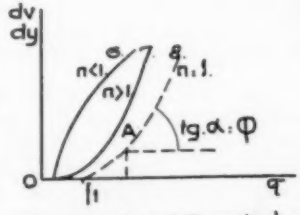
Curves 2 and 3 and also partly the portion OA of curve 4:

$\frac{dv}{dy} = \psi\tau^n$ ψ fluidity = $\frac{1}{\eta}$

Rectilinear portion of curve 4:

$\frac{dv}{dy} = \varphi(\tau - f)$.

e.



Curves 6 and 7 and also partly f_1A of curve 8.

$\frac{dv}{dy} = \psi(\tau - f)^n$

φ = fluidity = $\frac{1}{\eta}$

Rectilinear portion of curve 8:

$\frac{dv}{dy} = \varphi(\tau - f)$

Fig. 5.

This definition of the word " plastic " has also been adopted by our co-operators Saal and Koens in previous publications.[3]

When calculations of viscosities are made below, based on the conventional consistency determinations—chiefly on the penetration—it should be borne in mind that, with the exception of the calculation of the purely viscous asphaltic bitumens, the viscosities thus calculated are never to be taken in the theoretical sense of the word, but that they are arithmetical magnitudes which will be indicated as " apparent viscosity." It may be highly useful to know these when studying the rheological behaviour of the bitumens.

Thus, the apparent viscosity will be calculated in the following pages from the penetration by the formula :

$$\eta = \frac{5{\cdot}13 \times 10^9}{\text{pen.}^{1{\cdot}93}} \text{ poises}$$

even if this refers to non-purely viscous asphaltic bitumens, although this equation only holds good for purely viscous asphaltic bitumens.

Saal and Koens (*loc. cit.*) write about this :

> " Thus the determination of the penetration may be conceived as a determination of the viscosity. If, however, a plastic asphaltic bitumen is under examination, this determination can at the most stand in relation to a kind of average viscosity. It is generally the custom to compare two asphaltic bitumens of the same penetration; the above formula now makes it possible to calculate from the penetration of the plastic asphaltic bitumen the viscosity of a non-plastic asphaltic bitumen of the same penetration. This calculated viscosity (which we shall henceforward indicate by $\eta_{\text{pen.}}$) can then be compared with the observed series of viscosities of the plastic asphaltic bitumen."

Therefore, when studying the theories in which use is made of this mathematical relation between penetration and viscosity, it should be realized that for asphaltic bitumens which have no purely viscous character, this means that at each temperature at which the penetration has been determined those values for the viscosity should be taken into account which purely viscous asphaltic bitumens would possess if they had the same penetrations at the same temperatures.

Recent investigations of our collaborators Adriani and Limburg [6] have shown that up to comparatively great deformations the rate of deformation continues to decrease under the influence of a constant-deforming force, owing to the elastic properties of the material, so that the viscosity does not reach a final value. During the determination of the penetration this minimum deformation required is certainly never attained (the point of the penetration needle can never reach this, as it is always applied to fresh, undeformed material); the influence of the elasticity is therefore never completely eliminated during the penetration determinations on elastic materials. This circumstance constitutes an additional reason for speaking of " apparent viscosity " in cases where the viscosity has been calculated from the penetration of non-purely viscous bitumens, which are always more or less elastic.

The question now arises: What can we learn from the temperature susceptibility of the penetration of asphaltic bitumens—on which a characterization could be based so important for the technical application of these products—about the temperature susceptibility of their apparent viscosity?

In equation (1) we saw that the relation between penetration and temperature is given by:

$$\log \text{pen.} = K_1 + \alpha t$$

By equalizing the apparent viscosity (η_a) to $\frac{5{\cdot}13 \times 10^9}{\text{pen.}^{1{\cdot}93}}$ the relation between η_a and the temperature would therefore be found to be:

$$\log \eta_a = K - 1{\cdot}93\, \alpha t.$$

Thus calculated, the degree of the temperature susceptibility of the penetration (α) would therefore be closely bound up with the temperature susceptibility of the apparent viscosity ($1{\cdot}93\alpha$) calculated from the penetration: the apparent viscosity curves of the asphaltic bitumens of the *R* type are therefore found to be considerably flatter than those of the normal type.

For a bitumen with index *O*: $-\frac{d \log \eta a}{dt} = 0{\cdot}077$

" " " " $+3{\cdot}8$: $-\frac{d \log \eta a}{dt} = 0{\cdot}045$

However, it should be borne in mind that when the penetrations of non-purely viscous asphaltic bitumens are determined at deviating temperatures and, consequently, at different penetration depths, the shearing stresses are different. Since the apparent viscosity depends on the shearing stress, this circumstance may give rise to erroneous conclusions about the changes in apparent viscosity as a function of the temperature.

For this reason one of our co-operators, Labout,[6] has ascertained the influence of alterations in the shearing stress at one given temperature, or, in other words, the penetration has been determined from a point where the needle had already penetrated into the bitumen over a certain distance. Practically, this works out to a determination of the penetration depth after different times of penetration. Of the resulting curves any desired portion can then be used.

The following bitumens have been examined:

	R. & B.	Pen./25° C.	Index.
I. A bitumen of the *Z* type with a purely viscous flow (steam-refined) . . .	43° C.	77	−2·2
II. A bitumen of the normal type (steam-refined)	48·7° C.	81·5	−0·2
III. A bitumen of the *R* type (blown) . .	65·7° C.	85·5	+3·8

(*N.B.* Asphaltic bitumens II and III were made out of the same crude, II by steam distillation, III by blowing.)

In the accompanying graph (Fig. 6) the relation has been plotted between penetration depth and penetration time of these three bitumens at 15 and

25° C.; from this graph it may be concluded that for these three bitumens there is a linear relation between the logarithm of the penetration depth and the logarithm of the penetration time. These lines differ in slope, which is steepest in the case of bitumen I—probably purely viscous—and least for the blown bitumen III of the *R* type.

Saal and Koens (*loc. cit.*) inferred that the following relation applies: (at one given load and temperature):

$$\text{pen.}^{1\cdot93} = \text{const.} \times \frac{t}{\eta}$$

where t = time of penetration.

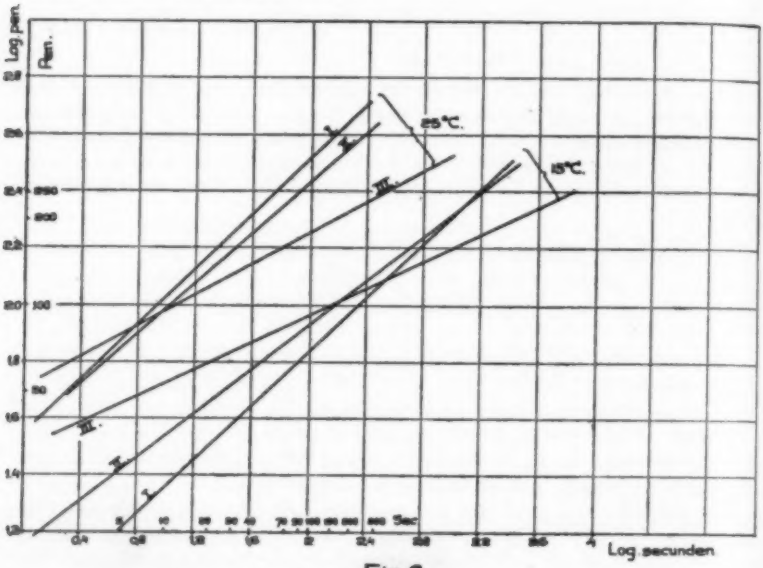


Fig. 6.
Relation between penetration and time of penetration of Asphalts I, II and III.

As for purely viscous bitumens, η is independent of the shearing stress, hence constant, this may be written:

$$1\cdot93 \log \text{pen.} = K + \log t.$$

The tangent of the angle of incline of the straight line indicating the relation between log pen. and log t for a purely viscous bitumen must therefore be $\frac{1}{1\cdot93}$; in the accompanying graph the tangent of the angle of incline of the probably purely viscous bitumen I is found to be $\frac{1}{2\cdot10}$.

For plastic bitumens η_a depends on the shearing stress, and the same formula gives:

$$1\cdot93 \log \text{pen.} = K_1 + \log t - \log \eta_a$$

With an increasing penetration the shearing stress decreases and η_{is} increases, so that for non-purely viscous bitumens :

$$\frac{d \log \text{pen.}}{d \log t} < \frac{1}{1{\cdot}93}$$

From Fig. 6 the following values are found for bitumen II of the *N* type :

$$\frac{1}{2{\cdot}58}$$

for the blown bitumen III of the *R* type :

$$\frac{1}{4{\cdot}29}$$

Labout argued as follows :

From the proposition that, when two bitumens have the same penetration depth after the same penetration time, the average apparent viscosity of these bitumens is the same under the prevailing shearing stress, it follows that at the same penetration depth (hence the same shearing stress), the time required to reach this given penetration depth is a gauge for the apparent viscosity.

By means of bitumen I, the viscosity of which is the same at every shearing stress, the average apparent viscosity of bitumens II and III can be calculated at any given shearing stress. The penetration of bitumen I at 25° C. and 5 minutes is 77. Hence, the viscosity is :

$$\eta = \frac{5{\cdot}13 \times 10^9}{77^{1{\cdot}93}} = 11{\cdot}7 \,.\, 10^5 \text{ poises.}$$

Under these conditions the average apparent viscosity of the bitumens II and III is about the same as that of bitumen I. If the penetration is taken at a lower shearing stress—say between 200 and 250 pen.—the time required for the penetration of the needle from 200 to 250 pen. is $22\frac{1}{2}$ minutes for bitumen I. Under these conditions R bitumen III requires 214 minutes and N bitumen II $33\frac{1}{2}$ minutes. The average apparent viscosity of the *R* bitumen under the prevailing shearing stress is, therefore :

$$\frac{214}{22\frac{1}{2}} \times 11{\cdot}7 \,.\, 10^5 \text{ poises} = 11{\cdot}1 \,.\, 10^6 \text{ poises, at } 25° \text{ C.}$$

For the normal bitumen II we find at the same shearing stress :

$$\frac{33\frac{1}{2}}{22\frac{1}{2}} \times 11{\cdot}7 \,.\, 10^5 = 17{\cdot}5 \,.\, 10^5 \text{ poises at } 25° \text{ C.}$$

At 15° C. the penetration of bitumen I during 5 seconds is $16\frac{1}{2}$, hence the viscosity is :

$$\frac{5{\cdot}13 \times 10^9}{16{\cdot}5^{1{\cdot}93}} = 22{\cdot}4 \,.\, 10^6 \text{ poises.}$$

If the penetration is again taken at a lower shearing stress, viz. between 200 and 250 pen., the time required for the penetration of the needle from 200 to 250 pen. for bitumen I is 590 minutes at 15° C.; for *R* bitumen III this time is 3795 minutes and for *N* bitumen II 664 minutes. The average

apparent viscosity of the *R* bitumen under the prevailing shearing stress is, therefore :

$$\frac{3795}{590} \times 22{\cdot}4 \times 10^6 \text{ poises} = 14{\cdot}4 \,.\, 10^7 \text{ poises},$$

and for the *N* bitumen $25{\cdot}3 \,.\, 10^6$ poises at 15° C.

When the apparent viscosity found at this shearing stress is substituted for that found by the normal penetration determination, the picture is quite different (see Fig. 7).

Although it must be assumed that, owing to complicating phenomena such as elasticity, the relation between the changes in penetration and in real viscosity under a constant shearing stress may be much more intricate than has been sketched here, the above exposition may yet give some general idea of the great influence of an alteration in the shearing stress on the viscosity calculated from the penetration values. Labout's approximate calculation, in which no account is taken of the elasticity, shows that a reduction in the shearing stress causes a substantial decrease in the great difference in steepness of the viscosity curves calculated from the penetration values at different temperatures for bitumen III and bitumen II.

The influence of the shearing stress on the temperature susceptibility of the apparent viscosity of non-purely viscous bitumens

$$\left(\frac{-\,d \log \eta_{ia}}{dt}\right)$$

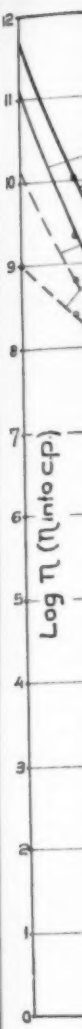
can also be seen from Table I.

TABLE I.

Viscosity Determinations on Blown Mexican Bitumen.

Temperature.	Determinations with the Couette Viscometer.		Penetration determinations.		
	F_1 = 11,300 dynes/sq. cm.	F = 22,600 dynes/sq. cm.	Penetration.	Lowest Shearing Stress at Penetration Needle in dynes/sq. cm.	Apparent Viscosity Calculated from the Penetration.
45° C.		65,000 K.P.	81	380,000	1,060 K.P.
					$-\frac{d \log \eta}{dt} = 0{\cdot}050$
50° C.	27,000 K.P.		108	270,000	600 K.P.
		$-\frac{d \log \eta}{dt} = 0{\cdot}120$			$-\frac{d \log \eta}{dt} = 0{\cdot}045$
					$-\frac{d \log \eta}{dt} = 0{\cdot}040$
55° C.	$-\frac{d \log \eta}{dt} = 0{\cdot}127$		139	220,000	380 K.P.
60° C.	1,460 K.P.	1,030 K.P.			

In this table have been listed the results of some Couette Viscometer determinations on blown Mexican bitumen (index about + 4·5). The



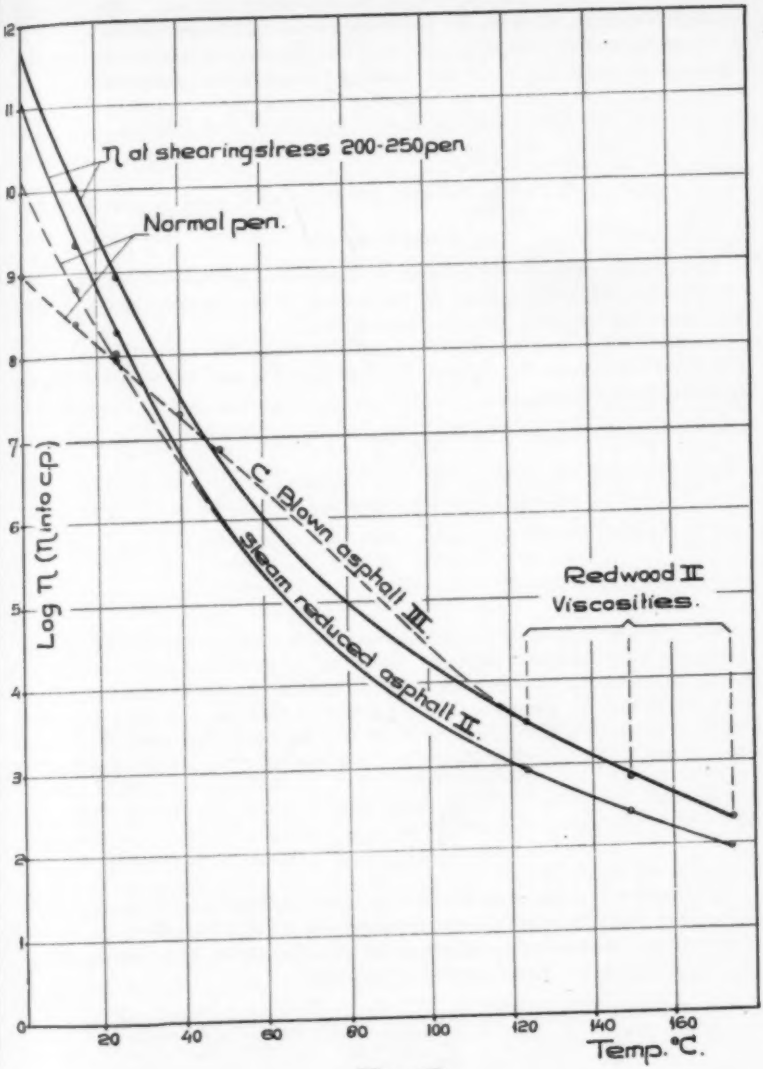


Fig. 7.

Viscosity-temperature curves of steam-reduced asphalt II and blown asphalt III.

determinations were made at two different shearing stresses. The apparent viscosities calculated from the penetrations have also been tabulated.

These figures show that the slope of the apparent viscosity curve found depends to a high degree on the shearing stress applied, namely :

$$\text{at } F_1 = 11300 \text{ dynes/sq.cm.}, -\frac{d \log \eta}{dt} = 0{\cdot}127$$
$$,, \; F_2 = 22600 \quad ,, \quad ,, = 0{\cdot}120$$
$$,, \; F_3 = \text{greater than } 200000 \quad ,, \quad ,, = 0{\cdot}045$$
(pen. determination)

That for the non-purely viscous products the temperature susceptibility of the viscosity must depend on the extent of the shearing stress applied becomes clear from the following argument :

Suppose that the viscosity of a plastic bitumen has been determined at the shearing stresses F_1, F_2 and F_3 ($F_3 > F_2 > F_1$) and at the temperatures t_1, t_2 and t_3 ($t_3 > t_2 > t_1$)

—	F_1	F_2	F_3
t_1	a_1	a_2	a_3
t_2	a_1'	a_2'	a_3'
t_3	a_1''	a_2''	a_3''

a = viscosity.

We saw above that both the viscosity determinations made by Saal on asphaltic bitumens and those by Houwink on synthetic resins invariably gave curves which were convex to the T axis in the shear–stress diagram, so that it may be assumed that for a plastic flow the viscosity decreases with an increasing shearing stress. It may be concluded from this—since we assumed $F_3 > F_2 > F_1$—that: $a_3 < a_2 < a_1$; as $t_3 > t_2 > t_1$, it also follows that :

$$a_1'' < a_1' < a_1$$
$$a_2'' < a_2' < a_2$$
$$a_3'' < a_3' < a_3$$

If t_3 has been chosen sufficiently high, there will probably be only a slight departure from the purely viscous behaviour at this temperature, so that the viscosity will be independent of the shearing stress, and, consequently, $a_1'' = a_2'' = a_3''$. Hence, (since $a_1 > a_2 > a_3$) :

$$\frac{(\log a_1 - \log a_1'')}{t_3 - t_1} > \frac{(\log a_2 - \log a_2'')}{t_3 - t_1} > \frac{(\log a_3 - \log a_3'')}{t_3 - t_1}$$

The temperature susceptibility of the viscosity is, therefore, greater at the shearing stress F_1 than that at F_2, and this, again, is greater than that at F_3.

The general rule, therefore, is that the temperature susceptibility of a plastic bitumen is always lower according as the viscosity curve has been determined at a greater shearing stress. The reduction in temperature

susceptibility owing to an increase in shearing stress will be an expression of the degree of plasticity of the material. For purely viscous bitumens the same temperature susceptibility is invariably found, no matter what shearing stress is applied.

For the purely viscous bitumens examined by us the slope of the viscosity line obtained from the penetration in the ordinary way is therefore an accurate gauge for the temperature susceptibility. The temperature susceptibility of the purely viscous bitumens examined did not, in general, differ very much, as may be seen from the table below :

	Pen./15° C.	Pen./25° C.	Pen./50° C.	Index.	$-\frac{d \log \eta}{dt}$.
Bitumen IV . . .	35	146	—	−2·7	0·120
Bitumen V . . .	20	79	—	−2·5	0·116
Bitumen VI . . .	—	2·5	62	−2·2	0·110

Bitumens with a slightly lower temperature susceptibility and an index of about 0, $\left(-\frac{d \log \eta}{dt} = 0{\cdot}077\right)$, such as soft, normal steam-reduced Mexican bitumens, already exhibit a dependence of the viscosity on the shearing stress, as was shown by Saal and Koens (*loc. cit.*) :

Determinations with the Couette Viscometer on Soft Straight-run Bitumen at 25° C.

F in dynes.	η (in K.P.).
610	258
1·220	250
2·440	246
12·200	218

Even for this soft steam-refined bitumen it must, therefore, be assumed that the viscosity curve is flattened in consequence of plasticity :

It must be concluded from the above that the differences in index or temperature susceptibility of the penetration between the bitumens of the different types are most probably, in the first place, attributable to the differences in the extent to which they deviate from the purely viscous behaviour.

It was observed above that the shearing stresses at which the apparent viscosity is determined in practical bitumen analysis deviate greatly. Although these shearing stresses greatly vary in different places in the trial patches, the order of magnitude of these shearing stresses, which mainly influence the result, can be indicated by the following rough figures :

Flow test *	100–500 dynes/sq. cm.
Redwood II Viscometer . . .	2×10^2 ,,
Sinker Viscometer	10^3 ,,
Melting point R. & B. . . .	10^3 ,,
Penetration 300	10^5 ,,
30	10^6 ,,
3	10^7 ,,

* In this test a thin (3–5 mm. thick) bitumen layer is applied to a flat iron sheet, and the displacement is measured of a point in the bitumen surface when the sheet is placed in a vertical position or at an angle of 45° with a horizontal plane, and heated for a given time (say 24 hours) at a given temperature.

The apparent viscosity temperature curve thus determined of a bitumen therefore gives viscosity values pertaining to greatly varying shearing stresses, in this sense—that in the direction of the lower temperatures the apparent viscosities are determined at a higher shearing stress. As deformation velocity $= \frac{\text{shearing stress}}{\text{viscosity}}$, and all viscosity determinations, to be applicable in practice, have necessarily to be carried out at deformation rates of approximately the same order of magnitude, or, at least, lying within certain limits, it is obvious that the shearing stresses applied must vary about proportionally to the viscosity.

The question is: what is the value of the apparent viscosity curve determined in the laboratory at such greatly deviating shearing stresses for estimating the utility for certain technical applications of asphaltic bitumens, the majority of which show plastic flow?

The answer to this question can be approached by considering that—also when used for technical applications—asphaltic bitumens must comply with the above relation between deformation rate, shearing stress and viscosity. Assuming that the deformation rates which these products should be capable of withstanding, at the different temperatures prevailing under technical conditions, will be of approximately the same order of magnitude, the shearing stresses occurring at these different temperatures will also vary approximately in proportion to the corresponding viscosities.

Consequently, when judging an asphaltic bitumen for the utility at low and at elevated temperatures, we are not interested in the viscosities at any given constant shearing stress, but rather in the apparent viscosities at shearing stresses, which vary approximately in proportion to the appurtenant viscosity. As we saw above, these are the apparent viscosities as found by the conventional methods. This comes to the fore, for instance, when judging the utility of a bitumen for the protection of pipe-lines, surface coats on roofing paper, etc.—in short, for those applications in which the bitumen, applied in a comparatively thick layer, must possess a sufficient flexibility at low temperatures (0° C.) and a sufficiently high viscosity at comparatively elevated temperatures (80° C.; the layer should not flow in the heat of the sun).

The rheological properties of such a bitumen composition will have to be studied at a low temperature (0° C.) under high shearing stresses, since the deformations to which these products are subjected in their technical applications at low temperatures bring about very great shearing stresses in the material. Consequently, when judging this bitumen composition for a technical application at 0° C., it is of importance to determine its viscosity at 0° C. *under a very high shearing stress.*

The viscosity at the highest temperature (80° C.) prevalent under technical conditions is, naturally, of importance only *when measured at a low shearing stress*; for, to find out whether the bituminous surface coats will flow, it is in this case necessary to know the viscosity under the shearing stress of the component of gravitation, which is very small.

It is clear that a viscosity curve measured over the temperature range 0–80° C. at a constant shearing stress would yield values for the viscosity which would be a much less reliable gauge for the practical utilization of

the bitumen at a low and at a high temperature (under a high and a low shearing stress, respectively) than the existing conventional viscosity curves.

The knowledge of the changes in apparent viscosity with the temperature and the shearing stress applied is certainly insufficient for a definite judgment of the suitability of asphaltic bitumens for the enormous variety of technical applications. Thus, for numerous industrial applications the suitability of the material will undoubtedly depend on the rheological behaviour under a comparatively slight deformation, and this behaviour is very largely, if not exclusively, determined by the elastic properties of the material.

To judge the suitability of asphaltic bitumens for technical applications, it is therefore of great importance to make a closer study of the rheological properties of asphaltic bitumens under a comparatively slight deformation. This means an investigation into the elastic properties of these materials, about which little has so far been published.

The Interior Structure of Asphaltic Bitumens.

The classification of asphaltic bitumens according to the angle of incline of the penetration curve between room temperature and the temperature of the melting point Ring and Ball—which, as was seen above, amounts to a classification based on the degree to which the viscosity depends on the shearing stress applied—must also fit in with the interior structure of asphaltic bitumens. That this is actually the case can be inferred from the following theories, which have been partly derived from Klinkenberg.

Before dealing further with their constitution, it should be noted that asphaltic bitumens are at present generally looked upon as colloidal systems.

Kalichevsky and Fulton [7] chiefly referring to Russian literature unknown to us, gave a survey of the development of the views regarding the constitution of asphaltic bitumens. In agreement with Sakhanov,[8] asphaltic bitumens are called colloidal solutions, in which the asphaltenes are lyophile with respect to the aromatic hydrocarbons and similar solvents, with which they form highly disperse and stable systems.

The first fully documented publication known to us about the colloidal structure of asphaltic bitumen is by Nellensteyn.[9] Of later publications which contain views on the constitution we mention those by C. Mack.[10]

It will appear from the subsequent pages that we largely subscribe to the opinions of the above authors, although in some respects the extensive data at our disposal may have led to more general conclusions.

The chemical research methods that have been applied to get an insight into the factors governing the constitution of asphaltic bitumens have, on account of the exceedingly complicated composition of these products and the slight chemical reactivity of the constituent hydrocarbons, in general contributed but little to enlarging this view.

An investigation in this direction was made at Amsterdam by our collaborator Eichwald,[6] who started from the observation that the cracking of coal-tar pitch gives a distillate consisting entirely of aromatics (soluble in furfural and sulphonatable). On the strength of this, an attempt was made to get an insight into the chemical nature (aromatic or

aliphatic) of certain fractions of the asphaltic bitumens by cracking them. Some preliminary experiments showed that in this manner something can actually be achieved.

For an efficient separation of the asphaltic bitumens into their components it has always been necessary to resort to physical methods, chiefly to the fractional precipitation.

Undoubtedly the most important separation is that into asphaltenes and maltenes. Asphaltenes are defined as the constituents which precipitate in weak dilutions with some low-boiling organic solvents, whereas maltenes are those constituents which dissolve in these solvents. The asphaltenes do not melt, but sinter together when heated, whilst the maltenes in a pure condition gradually soften on being heated.

However, together with the asphaltene proper (in a more absolute sense), various other constituents precipitate, according to the nature of the precipitating agent. It has not been found possible so to remove these that the same final product is retained. It should therefore invariably be stated how the asphaltenes have been obtained. In this way, the ether asphaltenes, the 60/80 asphaltenes (obtained by precipitation with aromatic-free gasoline, boiling range 60–80° C.) and the pentane asphaltenes are more or less sharply defined products. Unless otherwise stated, asphaltenes are in the following pages understood to be 60/80 asphaltenes.

It should be noted here that Marcusson [11] distinguishes, in addition to asphaltic acids and their anhydrides, three groups of constituents, namely:

1. *asphaltenes*, part insoluble in low-boiling petroleum ether;
2. *asphaltic resins* (Erdölharze), that part of the petroleum ether extract which is absorbed by fuller's earth;
3. *oily constituents* (ölige Bestandteile), that part of the petroleum ether extract which is not absorbed by fuller's earth.

Mack, too (*loc. cit.*) agrees with Marcusson in distinguishing "asphaltenes," "asphaltic resins" and "oily constituents."

The fraction denoted below as maltenes is therefore the mixture of asphaltic resins and oily constituents.

As the asphaltenes do not melt, but the maltenes, on the contrary, behave as viscous oils which constantly become more thinly liquid when heated, it is natural to look upon the asphaltenes as the very high molecular hydrocarbons, which are dispersed as particles of colloidal size in the much lower molecular hydrocarbons of the maltenes.

Nellensteyn (*loc. cit.*) groups the asphaltic bitumens with the protected lyophobe sols. As such he distinguishes three groups of components:

1. the medium
2. a lyophile part: the protecting bodies
3. a lyophobe part: the ultramicrons, consisting of elementary carbon.

In our view it is unproved, and, on the strength of ultramicroscopical examination, scarcely likely that the micella nucleus of the disperse phase should consist of elementary carbon. This point is, however, of only minor importance, for a correct insight into the constitution, since physically

—for instance in their stability—these systems behave as colloids of a preponderantly lyophile character.

The splitting of the asphaltic bitumens into asphaltenes and maltenes has rendered it possible to make a closer study of the influence of the properties of the dispersed phase and of the dispersion medium on the properties of the colloidal system, the asphaltic bitumen.

By means of 60/80 gasoline we separated the asphaltenes from the maltenes of three asphaltic bitumens, A, B, C, of which :

A = a high-temperature susceptibility bitumen of the *Z* type (with a truly viscous flow);
B = a steam-refined bitumen of the normal type (hardly plastic);
C = a blown bitumen of the *R* type (very plastic).

The maltenes of these three asphaltic bitumens proved to be purely viscous; plasticity could not be noticed in any of these cases.

When in these three types of maltenes the same type of asphaltenes was dissolved, the maltenes ex bitumen A yielded a bitumen with a purely viscous flow, maltenes ex B a bitumen with a slightly plastic flow of the normal type and the maltenes ex C a bitumen of the *R* type with great plasticity.

The rheological behaviour of the colloidal system—as expressed by the relation between penetration and melting point R. & B. or by the slope of the penetration curve—chiefly depends therefore on the properties of the continuous phase; in addition, the quantitative relation between continuous and disperse phase plays a part, inasmuch as with an increasing asphaltene content the viscosity of the system becomes greater.

We consider the asphaltenes as high-molecular hydrocarbons of a predominantly aromatic or hydro-aromatic character with a comparatively low hydrogen content, formed by polymerization and dehydrogenation from lower-molecular hydrocarbons. It is self-evident that the aromatics and hydro-aromatics must chiefly be held responsible for the formation of asphaltene micellæ, seeing that the aromatic and hydro-aromatic hydrocarbons exhibit a much greater chemical reactivity than the aliphatic.

Postulating that the surface of the asphaltene micellæ is aromatic or hydro-aromatic in nature, it is to be expected that these will " dissolve " or peptize best in aromatic or hydro-aromatic maltenes. Since the asphaltic bitumens of the *Z* type (unlike those of the *R* type) are purely viscous, so that it must be assumed that the asphaltene micellæ do not hinder each other's motion in flow, and, consequently, that they are well peptized, it is plausible, in connection with the above, that the maltenes of these asphaltic bitumens will be of an aromatic or a hydro-aromatic character. In agreement with this, the crude oils which yield bitumens of the coal-tar pitch type are typically aromatic or hydro-aromatic in nature, and give, for instance, highly temperature-susceptible lubricating oils; the highly aromatic coal-tar pitch, with its purely viscous flow, also furnishes an example of complete peptization in an aromatic medium.

If, on the contrary, the aromatics or hydro-aromatics, which are good peptizing agents, are removed from the maltenes—for instance by blowing (owing to which they themselves are converted into asphaltenes)—there is no longer complete peptization of the asphaltenes, but these will then adhere

to each other in a more or less flocculated condition, so that their free motion is impeded. A purely viscous flow is then out of the question; we get a picture of the plastic flow of the bitumens of the *R* type.

The peptizing power of the maltene fraction depends, in addition to the quantity of the aromatics and hydro-aromatics, also on the manner of distribution over the fractions of different molecular size.

Indications have been obtained that especially the high-molecular aromatics have a dominating influence on the peptization of the asphaltenes.

Base materials which, when blown, show a rapid decrease in viscosity of the maltene fraction—so that evidently the asphaltene formation chiefly takes place at the cost of high-molecular aromatics—are characterized by great differences between the rheological properties of the blown and of the straight-run products. These differences are, on the other hand, much

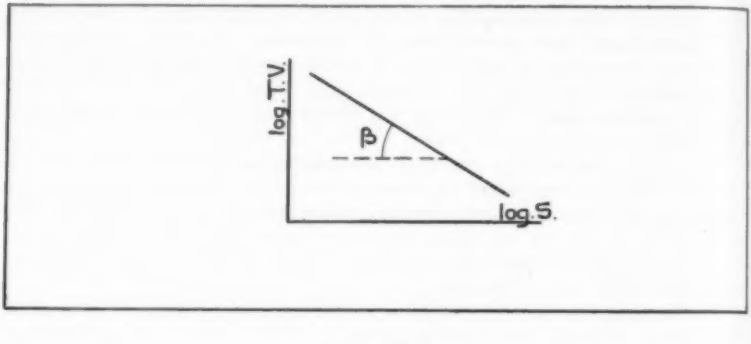


Fig. 8.

Relation between the logarithms of the turboviscosity and of the falling velocity.

smaller in the case of base materials the maltene fraction of which changes comparatively little in viscosity by blowing, and the aromatics or hydro-aromatics of which must therefore be of a smaller average molecular size.

The peptizing and flocculating conditions of the asphaltenes in a medium of lower-molecular hydrocarbons can best be studied from bitumen solutions in different solvents. For this reason, we shall discuss some properties of these bitumen solutions.

When a bitumen of the *R* type is dissolved in a petroleum fraction with a boiling range of 140–200° C. (white spirit) in the ratio of one part of bitumen to one part of solvent, and the solution is allowed to stand for some time, its viscosity is generally observed to depend more or less on the shearing stress applied. This is expressed by saying that the bitumen solution has gelatinized.

The gelatination phenomena of these bitumen solutions has been studied by our collaborator, Stern,[12] by means of a Wolff–Höpke turboviscometer. The viscosity is determined by allowing a stirring blade of a given shape,

which is driven by a drop weight on a cord wound round the axis of this stirring blade, to rotate in the bitumen solution under test, and then measuring the falling velocity of the weight.

The turboviscosity (T.V.) is given by the relation :

$$\text{T.V.} = \frac{\text{weight} \times \text{time of falling for a distance of 1 m.}}{100} = \frac{gt}{100};$$

the rate of falling $S = \frac{100}{t}$ cm. per second.

The turboviscosity of the bitumen solutions is determined at different, increasing rates, hence at increasing shearing stresses, whilst the temperature is kept constant. The turboviscosity of non-gelatinized liquids, such as water, glycerine and lubricating oil, proves to be independent of the rotation velocity of the blade, hence independent of the shearing stress, whereas that of the gelatinized solutions decreases greatly with an increasing shearing stress. It is found that there is a linear relation between the logarithm of the turboviscosity and the logarithm of the falling velocity (see Fig. 8), so that tan β is indicative of the degree of gelatination (tan β for non-gelatinized solutions being $= 0$).

For a large number of solutions of asphaltic bitumens of the gelatinized type the degree of gelatination was studied by measuring tan β; this gives rise to the following comments :

1. The gelatination of the bitumen solutions is greater according as the bitumen is of a more pronounced *R* type. This confirms the above hypothesis that in the maltenes of the blown bitumens few molecules are present with good peptizing properties.

2. The aromatic content of the solvent has a very great influence on the degree of gelatination. Aromatic solvents such as benzene and solvent naphtha yield very well peptized, practically non-gelatinizing solutions; those of mineral turpentine (white spirit) do so to great extent. From several white spirit samples it appears that those with the highest aniline point, hence with the lowest aromatic content, invariably yield the most highly gelatinizing solutions. This is a strong indication of the aromatic character of the asphaltene surface.

3. In general, the solution shows the greater gelatinizing effect according as the asphaltene concentration is higher. As the gelatination, expressed as tan β, is an expression for the degree to which the micellæ hinder each other's flow, this result was to be expected.

4. Both the viscosity (T.V.) and the gelatination (tan β) increase with the age of the solution. Both may become so great by using a low aromatic solvent that the solution is no longer a sol, but has become a gel in every respect. This might be conceived by assuming that in the low aromatic medium, in which the peptization of the asphaltenes is highly incomplete, a constantly increasing flocculation takes place in course of time, *i.e.* the asphaltene micellæ associate to large aggregates, enclosing the molecules of the continuous phase until, finally, the continuous phase is entirely confined in them.

Such strongly gelatinized bitumen solutions are sometimes thixotropic, often very elastic and not infrequently subject to syneresis (contraction of the gel whilst pressing out the solvent).[13]

5. By the addition of a very large quantity of aromatic-free solvent, say 60/80 gasoline, the asphaltenes (even those from the bitumens of the *Z* type, which are thoroughly peptized) are precipitated. It is on this principle that the asphaltene determination is based. In view of the above it is clear that, when the aromatic molecule concentration in the continuous phase becomes too low owing to a great dilution with a non-aromatic solvent, the peptization of the asphaltene micellæ will be slight, so that flocculation will readily take place in the medium of low viscosity.

These hypotheses on the bitumen solutions hold, without alteration, for the asphaltic bitumens themselves. Here, too, the rheological behaviour of the colloidal system is governed by the degree of peptization of the particles of the disperse phase. We assume the bitumens of the *Z* type to be completely peptized sols, those of a pronounced *R* type to have a gel structure.

The colloidal dispersions in which the particles of the dispersed substance and those of the dispersion medium differ only in degree of condensation or polymerization, and in which a continuous series of molecules of every possible order of magnitude occur, are called isocolloidal dispersions by Wo. Ostwald [14] and R. Houwink (*loc. cit.*), and distinguished by the latter as *iso*sols and *iso*gels. As in the asphaltic bitumens molecules of a different composition (aliphatics, naphthenes, aromatics) from polymer homologous series occur, we shall, with Houwink, denote these systems as mixed *iso*sols or mixed *iso*gels.

The above data lead to the assumption that with gelatinized bitumens of a pronounced *R* type the asphaltenes form a sort of skeleton, and this skeleton formation must naturally give rise to elastic properties.

The bitumens of the *Z* type actually differ widely in elastic properties from the gelatinized bitumens of a pronounced *R* type.

Our collaborators Adriani and Limburg [6] have deformed a bitumen of a pronounced *R* type under the influence of a constant shearing stress, which can be done in a torsion apparatus [15] or in a tube viscometer (in which a bitumen column is shifted by hydraulic pressure in a glass tube and the flow rate is measured).

These experiments showed that :

1. The deformation rate under a constant deforming force is very great at first; it gradually decreases, but even after a very long time it has not yet reached a constant final value;

2. If, after the bitumen has been deformed for some time, the shearing stress is reduced to 0, the bitumen " resiles " over a considerable distance (see also Saal, *loc. cit.*). The decrease in deformation rate period may be accounted for by assuming that elastic counter-forces are called into action during the deformation process; these counteract the shearing stress applied, so that the remaining deforming force = shearing stress applied minus the elastic counter-tension.

Some bitumens of the *Z* type showed no or at most only a slight elasticity. The latter was only occasionally the case, and then only below 25° C. As one of these bitumens contained about 40 per cent. of asphaltenes, it follows that the elasticity, as found with the bitumens of the *R* type (and to less extent

also with those of the normal type), is not a function of the asphaltene content as such, although, naturally, the presence of a certain quantity of asphaltenes is an essential condition for the skeleton formation and, consequently, for the elastic properties.

In the light of the above hypotheses on the structure it is clear that we ascribe these differences in elastic properties to differences in peptization of the asphaltenes, and that we attribute the generation of the elastic counter-forces, which reduce the deformation rate and cause resilience after removal of the deformation tension, to the deformation of the building materials for the gel structure: the aggregates of flocculated asphaltene micellæ, which enclose molecules of the continuous phase.

Summary.

1. The asphaltic bitumens may be conceived as colloidal systems. The disperse phase, *i.e.* the asphaltenes, consists of high-molecular hydrocarbons of a predominantly aromatic character with a comparatively low hydrogen content, formed by polymerization and dehydrogenation from lower-molecular hydrocarbons. It is immaterial for present purposes whether this view is accepted or that of Nellensteyn, who considers the asphaltene micella to be a carbon nucleus enveloped in hydrocarbons.

2. The peptization of these asphaltenes is better according as the dispersion-medium is more aromatic or hydro-aromatic in character.

3. In bitumens produced from oils rich in aromatics or hydro-aromatics the asphaltenes may be peptized so well that the flow of these materials complies with Poiseuille's law, so that their viscosity is independent of the shearing stress applied (purely viscous *Z*-bitumens). With a somewhat lower peptizing power of the maltene fraction the products begin to exhibit a somewhat plastic character (normal type). When the peptizing power of the maltenes is lower still—due either to a low aromatic content of the crude, or to elimination of the aromatics or hydro-aromatics by blowing—the resulting bitumens have a strongly plastic character, which means that the viscosity largely depends on the shearing stress applied.

4. The degree to which the rheological behaviour of these different types of products deviates from the purely viscous type finds expression in the angle of incline of the penetration–temperature curve or in the "susceptibility to temperature change" of the bitumen, in this sense that, in general, the plastic character is more pronounced according as this angle (and, consequently, the "temperature susceptibility") is smaller.

5. With the aid of the index nomogram referred to in the paper, this "temperature susceptibility" of a bitumen can be expressed by a figure which we have called "index," when the penetration at 25° C. and the melting point Ring and Ball, or the penetration at any two different temperatures are known. In proportion as the index of a bitumen is higher, the angle of incline of the penetration–temperature curve is smaller and, consequently, the plastic character more pronounced.

6. When judging of asphaltic bitumens for their suitability in practice it is important to have them classified according to their "temperature susceptibility," expressed by an index. As we saw above, under point 4, this index practically indicates the degree to which the rheological behaviour

of these products deviates from that of the purely viscous type, and, according to 3, the differences in degree of peptization of the asphaltenes. This classification may therefore also be looked upon as being based on the degree of gelatination of these products.

7. The asphaltic bitumens with a high index are to be considered as mixed *iso*gels, *i.e.* as systems with a more or less coherent skeleton. They display typical gel properties, such as elasticity, syneresis and sometimes thixotropy. The lower the index of the product, the slighter the coherence between the building materials (asphaltenes) of the skeleton; in the bitumens of the *Z* type the gel properties such as elasticity, syneresis and thixotropy are almost entirely absent.

8. The working hypotheses evolved here give an idea of the constitution of asphaltic bitumens which, broadly speaking, makes it possible to understand the widely deviating rheological behaviour of the different types of these complicated hydrocarbon mixtures.

Laboratory,
N.V. De Bataafsche Petroleum Maatschappij.

Amsterdam,
S. 13th June, 1935.

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[12] W. Stern, in preparation.
[13] For definition and description of synaeresis see: H. Freundlich, *Kapillarchemie*, Leipzig, 1932, II, 642.
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OBITUARY.

CONRAD SCHLUMBERGER.

MR. CONRAD SCHLUMBERGER was born in 1878 in Alsace, and went to Paris at the age of sixteen. He distinguished himself both in classics at his "Lycée," later in pure science at the "Ecole Polytechnique," and finally in science applied to industry, at the "Ecole Supérieure des Mines de Paris."

Having been appointed Engineer to the State Mining Corps, he became rapidly noted for his attachment to scientific work, and at the age of twenty-nine was called to the Chair of Physics at the Ecole Supérieure des Mines de Paris, which he had left as a student only a few years before.

This nomination was the turning point of his scientific career. The idea of applying his knowledge of the science of physics to the art of mining led him to conceive, study, and finally evolve a new branch of science which consists in studying the underground to considerable depths, by physical studies carried out at the surface.

This problem can be studied by means of several physical properties of rocks. After careful consideration, he decided to chose their electrical resistivity, since this lends itself to precise measurements, and seemed likely to allow the study of a wide variety of geological problems, and this moreover without the further element of chance presented by the necessary creation of entirely new instruments.

As early as 1912 the theory, its experimental verification, and the necessary apparatus were sufficiently perfected to permit actual practical surveys, during the free time between college terms.

His studies in 1912, 1913 and 1914 in the Calvados Silurian Basin (France) constitute, as far as is known, the first tectonical studies carried out in the world by geophysical methods, using artificial fields of force.

His studies in the Sain-Bel (France) and Bor (Servia) ore deposits, carried out at the same period, showed that the vague ideas of a few forerunners to locate ore deposits by their electrical conductibility, had been transformed by him into an effective technique.

They also showed how a great scientist, coming across an anomaly in his measurements, can study and finally make it serve a useful purpose. For it was thus that Conrad Schlumberger discovered the spontaneous polarization created by ore deposits, and evolved therefrom a rapid and reliable prospecting method, which, applied in 1913 at Bor, led to what is probably the world's first geophysical discovery of a non-magnetic ore deposit.

When in 1914 his research was interrupted by the World War, a reliable and adaptable geophysical method had been created, and its possibilities tested in concrete cases, both for the study of sedimentary basins and the location of ore deposits.

The war years having been spent at the front as an artillery officer, it was not until 1920—that is to say, after a lapse of six years—that Conrad Schlumberger was able to publish the result of his remarkable studies, in a paper edited by Gauthier-Villars (Paris).

At this time he resumed his scientific studies, in collaboration with his brother Marcel Schlumberger, and continued with ever-increasing success to develop the work so auspiciously started.

As early as 1922 the idea of "apparent resistivity," which was rapidly applied to all the problems, simplified the interpretation, and led to the possibility of systematic geological studies over large areas. The idea of "investigation depth" was subsequently developed.

In 1923 a first general survey in connection with oil led to the proving of the existence, and the mapping, of the Aricesti dome, in the Rumanian plain.

By continual technical improvements he developed, varied and perfected the method which he had created, rendering it more and more adaptable in practice, at the same time training a number of young collaborators.

In 1928 the application of electrical measurements to the study of formations encountered by drill holes took form. The utilization of this technique in the stead of core-taking by mechanical means (more especially in oil wells) constituted such a marked progress that, in spite of prevailing industrial conditions, its application became generalized with unbelievable rapidity. There is scarcely an engineer or geologist the world over at the present moment who does not rely on these measure-

ments (which they have dubbed "a Schlumberger") for rational well drilling and exploitation.

Conrad Schlumberger died suddenly in Stockholm on May 9th, 1936, while still most actively engaged in his work. Besides his outstanding intelligence, his inventive and creative genius, he also possessed a natural kindliness and charm of manner which endeared him to all with whom he came in contact, and particularly to geophysicists of whom he was one of the foremost pioneers. M. S.

ERRATA.

"Characteristics of Solvent-refined Motor Oils." *Journal*, February, page 66.

Table III, Line 5, should read :

Viscosity Index	120	97	101	81	100	77	102	97	102	97

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

MEETING IN HOLLAND, MAY 1936.

INTERNATIONAL co-operation in all matters pertaining to petroleum technology was the keynote of the first overseas meeting of the Institution of Petroleum Technologists, held in Holland on May 8th–11th, 1936. This idea was underlying all the speeches at the technical sessions, the banquet and the luncheons. It found practical expression in the valuable personal contacts established between the technicians of the different countries represented at the meeting.

The Institution was the guest of the Koninklyk Instituut van Ingenieurs (Royal Dutch Institute of Engineers). Every member of the party had nothing but praise for the wonderfully organized programme arranged by the Reception Committee. No detail was overlooked which could possibly contribute to the pleasure and comfort of the visitors. At the technical session an important series of papers was presented dealing with diesel fuels and diesel engineering.

Eight countries were represented by the membership of the meeting—Holland, Great Britain, Denmark, France, Germany, Japan, Sweden, and U.S.A. The complete list of those who participated in the meeting is as follows :—

Prof. L. A. van Royen (President, Royal Dutch Institute of Engineers and Chairman of Reception Committee), Prof.-dr.-ir. H. I. Waterman, Hon.Mem.Inst.P.T. (Vice-Chairman, Reception Committee) and Mrs. Waterman, Ir. Wouter Cool (General Secretary, Royal Dutch Institute of Engineers and Honorary Secretary, Reception Committee) and Mrs. Cool, Ir. J. H. C. de Brey and Mrs. de Brey, Jhr.-ir. C. E. W. van Panhuys (Hon. Treasurer, Royal Dutch Institute of Engineers) and Freule. van Panhuys, Ir. H. Sangster and Mrs. Sangster, Dr. A. E. Dunstan (Past-President, I.P.T.), Mr. J. Kewley (Past-President, I.P.T.), Mr. S. J. Astbury (Secretary, I.P.T.).

Dr. F. H. Garner, Mr. A. C. Hartley, Prof. V. C. Illing and Mrs. Illing, Mr. J. S. Jackson, Dr. E. R. Redgrove (Members of Council).

Mr. W. C. Asbury (U.S.A.), Ir. J. A. Beukers (Holland), Ir. G. D. Boerlage, Ir. V. J. P. de Blocq van Kuffeler (Director-General of the Zuider-Zee Works), Ir. J. J. Broeze, Dr. H. L. Buning (Germany), Prof. Ir. M. H. Caron (Delft University), Ir. G. J. L. Caviët (General Manager, B.P.M. Laboratories, Amsterdam), Eng.-Comm. R. Enomoto (Imperial Japanese Navy), Mr. P. N. Everett, Mr. J. Filhol (Secretary, Association Française des Techniciens du Pétrole), Mr. G. W. E. Gibson, Ir. D. Goedkoop, Jr. (Messrs. Kromhout), Prof. Ir. J. A. Grutterrink (Professor of Geology, Delft University), Dr.-Ing. A.

Hagemann (Berlin), Dr. Heinrich, Ir. W. Hupkes (Netherlands Railways), Mr. C. C. Jacobs, Mr. H. F. Jones and Mrs. Jones, Mr. W. Kay and Mrs. Kay, Mr. H. G. Koefoed (Denmark), Mr. C. W. Knighton and Mrs. Knighton, Mr. D. J. W. Kreulen, Mr. L. J. Le Mesurier, Mr. J. J. Leendertse, Mr. van Leer, Mr. E. E. Manning and Mrs. Manning, Mr. N. Mitchell, Mr. P. C. Pope (Secretary, The Institute of Fuel), Mr. I. J. F. Reydon, Mr. R. Stansfield, Mr. D. A. Shepard (U.S.A.), Ir. H. W. Slotboom, Mr. L. C. Stevens, Mr. R. F. Sundstrom, Mr. H. C. Tett, Mr. R. Tillman, Mr. G. Voogt, Mr. H. N. de Wilde and Mrs. de Wilde, Dr.-Ing. O. Zaepke (Director, Deutsche Gesellschaft fur Mineralölforschung).

The Royal Dutch Institute of Engineers placed their commodious premises at 23 Prinsessegracht, The Hague, at the disposal of the visitors. The technical sessions were held in their lecture hall. Members of the Institute's staff were at the service of the visitors to render every possible assistance. A room had been reserved for the use of members of the Council of the I.P.T.

Official Welcome at The Hague.

The proceedings opened on Friday morning, May 8th, with a Reception by Prof. L. A. van Royen, Prof. and Mrs. H. I. Waterman, and Mr. and Mrs. W. Cool. The visitors (twenty-five of whom had travelled overnight from London) were entertained with light refreshments and had the opportunity of meeting their Dutch colleagues.

Prof. L. A. van Royen then welcomed the English visitors in the following gracious speech :

" The science of petroleum is of such importance to-day that no single state can close its eyes to the enormous interests which it embraces and serves. It has become both an object of incessant care for the respective governments, and a source of mental and practical labour for innumerable heads and hands.

" The Institution of Petroleum Technologists occupies a leading position in this field. I am a layman as regards the greater part of this science, and am not perhaps fully able to praise those who in 1914 founded the Institution, nor those whose names come to us from overseas as being exceptionally able pioneers and organizers who have placed the Institution on the high level at which it now stands.

" But I must mention here that we Dutch, who have some knowledge of petroleum technology, have the utmost admiration for the work of your Institution.

" The *Journal* of your Institution not only gives us a continued series of important articles on the most divergent subjects concerning petroleum, but the Addresses of its distinguished Presidents illustrate the importance of the petroleum industry in the world economy.

" The Royal Dutch Institute of Engineers is an organization which includes as members the majority of Dutch engineers. Amongst them there are many who have devoted their lives and intellects as technologists in the petroleum industry. Therefore it is for me, as President of the

Royal Dutch Institute of Engineers, a great privilege, and at the same time a great pleasure, to be able to welcome you all on Dutch soil. We very much enjoy meeting you all here to-day, to discuss with us some of the interesting problems which this industry produces in such an unlimited number.

"The fact that twenty-five of the members of your Institution are resident in Holland proves the friendly relationship which already exists between our organizations, and I sincerely hope that you will feel yourselves at home during your stay in this country. We assure you that we shall be only too glad to hear any of your wishes in order that we can try to comply with them.

"You have come to Holland in a month considered the most beautiful of the year. Spring has burst the buds of the trees and flowers. Our wide meadows, bulb-fields and broads are alight with brilliant colour. I trust that our climate, fickle as it likes to be, will show its best side to you, our guests, and allow you to enjoy your excursions under the most favourable conditions."

Dr. A. E. Dunstan (Past-President), in reply, said that it was with the very greatest regret that the President of the Institution, Sir John Cadman, was prevented from being with them that morning. Sir John had followed the preparations for the meeting with the keenest interest, and was extremely disappointed that circumstances had rendered it impossible for him to participate in its pleasures. On behalf of Sir John Cadman and the members of the Council of the Institution, Dr. Dunstan expressed their appreciation of Prof. van Royen's gracious welcome, and assured him that the members of the Institution of Petroleum Technologists were honoured to meet their Dutch colleagues under the ægis of the Royal Dutch Institute of Engineers.

Prof. H. I. Waterman then took the Chair to preside over the technical sessions. Before inviting the first Paper, Prof. Waterman welcomed the ladies, and expressed the wish that the programme arranged especially for the ladies would bring them many pleasant hours during their stay in Holland.

The ladies then left the meeting for a tour of The Hague and Delft, which had been arranged by Mrs. Waterman, Mrs. Cool, and Mrs. Sangster.

The following Papers were then presented by their authors and followed by a discussion :

"General Description of the Work carried out at the Proefstation of the Bataafsche Petroleum Maatschappij, Delft." By Ir. G. D. Boerlage.

"The Correlation of Tests on the Ignition Quality of Diesel Fuels, carried out at Delft and Sunbury." By G. D. Boerlage, Ir. J. J. Broeze, L. J. Le Mesurier and R. Stansfield.

The morning session finished at 1 p.m., and an adjournment was made to the Vieux Doelen Hotel, where the restaurant had been reserved for an informal luncheon. At 2.30 p.m. the party left by motor-coaches for Delft, proceeding first to the Proefstation of the Bataafsche Petroleum Maatschappij.

Visit to Delft Proefstation.

At the Delft Proefstation Ir. J. H. C. de Brey, Mr. G. D. Boerlage and their colleagues had organized an important and interesting series of demonstrations. Taken in conjunction with Ir. Boerlage's paper at the morning's technical session, these enabled the visitors to obtain a very complete view of the experimental work on engines and fuels carried out at Delft. The following details of the demonstrations are taken from the leaflet specially printed by the company for their visitors :

(1) *Ricardo E 35—"Delft" Piezo Electrical Indicator.* Detonation diagrams. Exhaust valve temperature measurement.

(2) *C.F.R. Engine.*—Determination of the "Allowable Boost Ratio" (A.B.R.) for high octane fuels.

(3) *Optical Observations of Combustion* in petrol engine (quartz windows) Flame photography. Spectography. Ignition from either end of combustion chamber. Temperature measurement by line reversal.

(4) *Research on Single-Cylinder Aircraft Engine.* Bristol Pegasus type. Air cooling by fan driven by Ford V8 engine. Supercharging by separate blower. Temperature measurement on sparking plug.

(5) *Various High-Speed Diesel Engines.—"Delft" Optical Indicator.* Delay measurements (cetene number). Direct injection : Gardner. Separate Combustion chamber : Ricardo. Pre-combustion chamber : Mercedes-Benz.

(6) *Various Small Gasoline and Diesel Engines* for duration tests on different fuels and lubricating oils. High temperature cooling.

(7) *Continuous Wear Measurement on Werkspoor Engine.* Air-injection diesel engine arranged for lacquer formation at low load.

(8) *Lacquer Formation in an Oil Engine.* Semi-diesel Gardner engine arranged for the purpose.

(9) *Measurement of Cetene Number* (ignition quality of diesel fuel). Thomassen diesel engine. Piston-type indicator.

(10) *Diesel Engine running on Extreme Residual Fuels.* Ricardo-type combustion chamber. Pre-heating of fuel. "Delft" nozzle cooling. No smoke, no carbon formation, yet highest B.M.E.P. on heaviest fuel.

(11) *C.F.R. Diesel Conversion.* Original turbulent head construction. Delay measurement by bouncing pin.

(12) *Chassis Dynamometer.* Correlation of octane number with practice.

(13) *E.P.L. and Oiliness Research.* Four-ball apparatus. Gear testing apparatus.

(14) *Kerosine Burners.* Improved blue flame-burner design. Kitchen stoves. Automatic hot-water supply. Draeger apparatus for measuring CO percentage.

After tea the visitors proceeded by motor-coach to the older parts of Delft, walked through the narrow, cobbled streets of the town which run alongside its quiet canals, and rejoined the coaches for the return to The Hague at about 6 p.m.

Visit to Delft University.

Meanwhile a smaller party had proceeded to the Delft University where they were received by Prof. H. I. Waterman (Chemical Engineering), Prof. Ir. J. A. Gutterrink (Geology), and Prof. Dr. C. Zwikker (Applied Physics).

A tour was first made of the Geological and Mineralogical Departments, where particular interest was taken in the X-ray crystallographic equipment, in the geophysical instruments and the records of geophysical work carried out by the department. The Geological Department of the University possesses a very complete and well-arranged geological and mineralogical museum. The visitors were indebted to Dr. P. Kruizinga, Conservator of the Museum, for an extremely interesting tour of this building.

In the Applied Physics Department Prof. Dr. C. Zwikker conducted the visitors over the sections devoted to high-tension researches and the acoustics department. The latter provided an interesting example of how a research method for one science can be adapted to another. An apparatus designed to test the sound-permeability of building materials was at once noted as applicable to the testing of the permeability of rocks to liquids. The visitors left the University of Delft greatly impressed by the magnificent equipment of these buildings and the important work which is being carried out on pure science research.

On Friday evening, May 8th, short lectures were given to the students of the Chemical Engineering Dept., University of Delft, by Dr. A. E. Dunstan and Mr. J. Kewley.

Technical Session, Saturday, May 9th.

Prof. H. I. Waterman presided over the technical session on Saturday morning, May 9th, when the following Papers were presented and discussed :—

"Diesel Rail Transport in the Netherlands." By Ir. W. Hupkes.
"The Design of Injectors for Diesel Engines." By Ir. A. Lugt.
"Different Methods of Assessing the Ignition Quality of Diesel Fuels." By Dr. F. H. Garner.
"Specification for Diesel Fuels." By C. H. Barton (presented in the author's absence by Mr. J. S. Jackson).
"Testing of Motor Fuels for the High-Speed Type Diesel Engine." By Dr.-Ing. A. Hagemann and Dr.-Ing. Th. Hammerich.

By courtesy of *Oel und Kohle* a summary of Dr. Hagemann's paper was available in both German, English and Dutch.

At the conclusion of the technical session an informal luncheon had been arranged at the Vieux Doelen Hotel. In the afternoon, which was free, many members took advantage of the opportunity to visit Scheveningen or to walk through the beautiful woods that lie between The Hague and the sea.

Banquet at The Hague.

On Saturday evening, May 9th, the visitors were entertained by the

Dutch petroleum companies to a banquet, held at the Hotel Witte Brug. The table, which had been arranged in the form of the "I" of "International," was charmingly decorated with masses of pink rhododendrons and tulips, and lighted by candles. An excellent orchestra provided a selection of Dutch, English, French, and German music throughout the evening.

At the beginning of the banquet, Prof. Waterman extended a welcome to the visitors and their ladies and proposed the health of "H.M. King Edward VIII." Mr. S. J. Astbury responded with the toast of "H.M. Queen Wilhelmina."

Later in the evening PROF. H. I. WATERMAN again addressed the gathering, and proposed the toast of the Institution in the following speech:

"Professor van Royen regrets very much that he cannot be present at this dinner. He has asked me to represent him this evening. I need not say that I do so with considerable pleasure.

"I have been a member of the Institution of Petroleum Technologists since 1923, in which year I first came in contact with Dr. Dunstan and Mr. Kewley. Since then I have always taken the greatest possible interest in its proceedings. The Council of the Institution of Petroleum Technologists is in every way representative of the whole science of petroleum in England.

"The Institution has brought us many good friends. The University of Delft has, on many occasions, been honoured by lectures from your Members of Council. Dr. Dunstan, a Past-President of the Institution, has been four times to Delft, and I can assure you that the students and graduates who have been present at his meetings doubly appreciate the cordial friendship which they receive from English petroleum technologists. I hope that these ties of friendship and co-operation will continue in the future, and if possible will become stronger. I trust that these meetings on Dutch soil and the banquet of this evening will increase and stabilize the good friendship between English and Dutch petroleum technologists. We all know the excellent work which the Institution has done in the past. We all believe that the members and future members will actively further its future development.

"It is a great pleasure and a great honour for me to propose the toast of the Institution of Petroleum Technologists."

DR. A. E. DUNSTAN, replying to the toast, said: "Prof. Waterman, Ladies and Gentlemen. Yesterday I made the apologies of Sir John Cadman for his absence on this very pleasant occasion. Had he realized that there would be here so much of wisdom and knowledge, so much of youth and beauty, he would have been doubly sorry that he could not be present.

"Now, I have been warned that this banquet would differ from our English way of doing things. I was told that in England the dinner was not so good, but the speeches were amazing, whilst in Holland dinner was marvellous, but there were no speeches at all. It is evident, therefore, that this is no occasion for a lengthy speech. However, there are certain very pleasant duties to perform. It would be exceedingly inappropriate if these were left undone. First of all, I have had a telegram

to-day from Sir John Cadman. He wishes hearty success to our gathering, and sends his good wishes to all our colleagues in Holland. I am sure I shall be voicing your own wishes when I suggest that we send him a telegram expressing our reciprocal greetings. If you agree, the words of this telegram will be :

> " Members of the Royal Dutch Institute of Engineers, of the Institution of Petroleum Technologists, their ladies and friends, send greetings on the occasion of the banquet at The Hague. This, the first occasion when the Institution has undertaken such a fraternal visit, has been marked by signal success."

(The proposal was carried with applause.)

" My next equally pleasant task is concerned with our Chairman, Prof. Waterman of Delft. It is no intention of mine to remind you that Prof. Waterman is supremely eminent as a man of science, a teacher and leader. This you all know. What I want to express is our admiration for him as President of our meetings—a model of kindness and courtesy. Prof. Waterman is one whom to know is to love and admire.

" To the Royal Dutch Institute of Engineers, represented here by their Secretary and their Treasurer, we owe more than I can express. Their hospitality has been impressive, and we are all deeply grateful to them. It was a special pleasure to have with us Prof. L. A. van Royen at our inaugural meeting. I should like particularly to say how much we appreciate the courtesy of the meetings conducted in the English language. To the great business organizations which, as always, have helped the Institution, not only financially, but also by an encouragement of their personnel to participate in its affairs, we gratefully acknowledge our indebtedness.

" I hope that all those who are here to-night representing the various companies will make a special point of conveying to their Directors our appreciation.

" To the readers of papers and those who have taken part in our discussions our thanks are due. A special vote of thanks must be given to those who have organized our excursions and who are endeavouring to show us as much as possible in our limited visit. I am sure the ladies will wish to be particularly associated with this expression of our gratitude.

" I should like to refer to our colleagues from other countries who have assisted at our meetings. M. Filhol is known to many of us. He comes with the satisfaction of knowing that L'Association Française des Techniciens du Pétrole is in a flourishing condition. May we hope that in the near future we shall all be able to avail ourselves of the opportunity of attending a corresponding meeting in Paris. I hope he will tell us something later on about the Second World Petroleum Congress. Herr Zaepke is very welcome here, with his colleagues from Germany. In that country is a prosperous Society of Petroleum Technologists. We deeply regret that Dr. Ubbelohde is prevented from being present this evening. Dr. Ubbelohde has sent me a telegram which I will read to you :

> " Zum groessten Bedauern bin ich ploetzlich an persoenlicher Teilnahme am Meeting in Holland verhindert. Der Tagung der englischen

und hollaendischen Mineraloelfachleute im Haag sende ich beste Wuensche fuer erfolgreiche Arbeit."

UBBELOHDE.

"I should like to end on a personal note. At our opening session I said that our Institution was international; that men of science and technology were, by training and temperament, international. This was evident in the free exchange of knowledge and experience—freely given and freely accepted. This meeting is an evidence of our faith.

"Prof. Waterman, I give you a toast that needs no reply. Ladies and Gentlemen, I ask you to drink with me to our technical and scientific bodies—to our men of science and technicians, whose devoted labours are putting at the disposal of mankind more and more knowledge—and we pray, more and more wisdom."

MR. J. KEWLEY proposed the toast of "The Ladies" in a witty speech, and particularly thanked those ladies who were making the stay of their English lady visitors so pleasant.

M. FILHOL, speaking in French, graciously thanked Prof. Waterman and the Royal Dutch Institute for their hospitality, and hoped the Association Française des Techniciens du Pétrole would have the pleasure of welcoming their friends of that evening on the occasion of the World Petroleum Congress in Paris in June 1937.

HERR O. ZAEPKE brought the greetings of the Deutsche Gesellschaft für Mineralölforschung, and looked forward to the continuance of that international co-operation in technical matters which had marked the technical sessions of the morning.

MR. H. G. KOEFOED (Denmark) referred with particular pleasure to the manner in which the representatives of the smaller nations were received on equal terms by those larger nations whose resources contributed to the development of petroleum science.

EXCURSION TO THE ZUIDER ZEE.

On Sunday morning, May 10th, the Management of the Netherlands Railways placed at the disposal of the party a diesel-electric train for the journey from The Hague to Amsterdam. Ir. Hupkes and members of the engineering staff of the Netherlands Railways received the visitors at the Hollandsche Spoor Station, and demonstrated details of the engine and motors, the coach equipment and driving-cab. During the course of the journey to Amsterdam every visitor had the privilege of sitting beside the driver in the driving-cab of the train, and watching the operation of the system of controls described in Mr. Hupkes' paper, while the train was actually travelling at speeds up to 110 kilometres per hour.

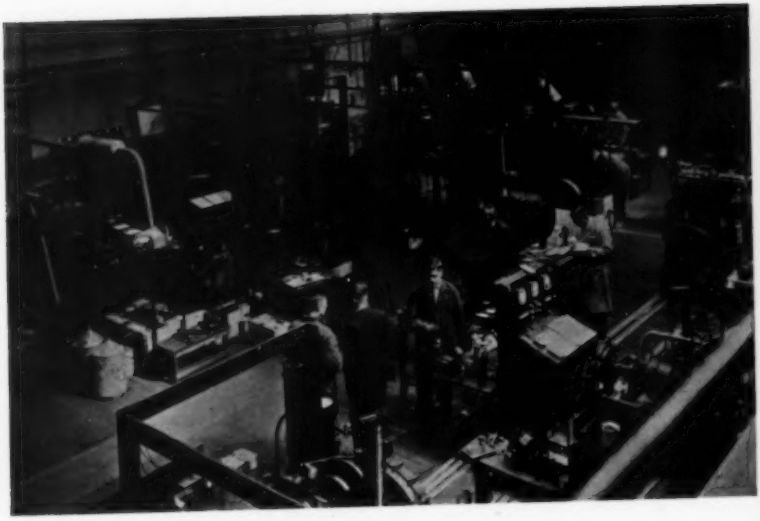
On arrival at Amsterdam the party was met by Mr. and Mrs. Cool and Mr. and Mrs. Sangster. Luggage was taken to the Carlton Hotel and the party transferred to motor-coaches for the excursion to the Zuider Zee. A special map of the route had been prepared by Mr. Sangster, and an interesting account of the Zuider-Zee reclamation works was given to the visitors by Mr. van Panhuys and Mr. Lugt.

A halt was made at 12 noon in the picturesque fishing village of Volendam,

GROUP OF VISITORS OUTSIDE THE DELFT PROEFSTATION.

[*To face p.* 450.

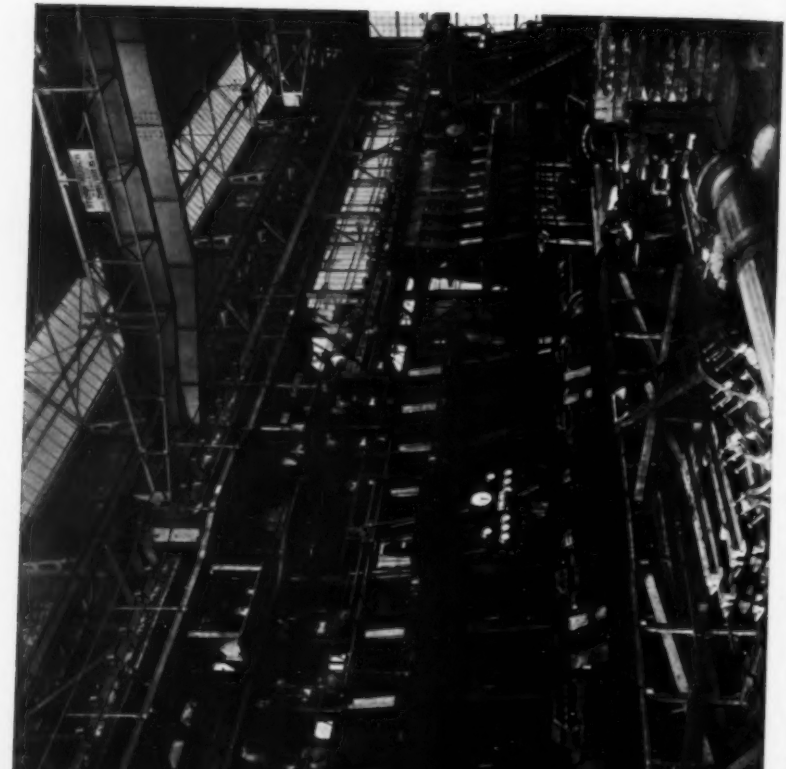
THE DELFT PROEFSTATION.



THE DELFT PROEFSTATION.

THE LABORATORIES, AMSTERDAM.

ONE OF THE LABORATORIES, AMSTERDAM.



EIGHT-CYLINDER MARINE DIESEL ENGINE ERECTED FOR TEST AT MESSRS. WERKSPOOR, AMSTERDAM.

where the arrival had been timed for the moment when the villagers were leaving church in their quaint Dutch costumes—affording a rich harvest of photographic subjects to those who had remembered to come provided with cameras.

From Volendam the route lay via Hoorn to the Wieringermeerpolder, the great area of approximately 45,000 acres which has been recovered from the Zuider Zee since 1932. Mr. van Panhuys explained the engineering problems which had been faced and the manner in which they had been overcome, as well as the human problems involved in the successful settlement of the land, and the varied agricultural and forestry problems connected with its development.

At Wieringermeer Mr. Lugt showed the visitors over the diesel-engined pumping-station, and demonstrated the starting up of one of the two large pumps, each having a capacity of 275,000 gallons of water per minute.

The journey was continued to the monument erected on the site where the sea dyke separating the North Sea from the Zuider Zee was closed in May 1932. A perfectly straight road with an excellent surface now runs parallel to the crest of the dyke connecting North Holland with Friesland, a distance of approximately 18 miles.

The return journey was made via Alkmaar and Zaandam to the Carlton Hotel, Amsterdam.

On Sunday evening, Mr. van Leer of Amsterdam invited the members of the party to a performance of his Circus "Kavaljos"—the Amateurs' Circus—specially arranged to mark the occasion of the Institution's meeting in Holland. At the conclusion of the circus performance he entertained the visitors in the adjoining hall, where dancing continued until the early hours of Monday morning. At breakfast on Monday every member of the party was presented with a charming souvenir of the Circus, in the form of a leather folder containing photographs taken the previous evening.

Visits on Monday, May 11th.

Monday morning, May 11th, was devoted to a visit to the Laboratories of the Bataafsche Petroleum Maatschappij. A motor-coach conveyed the party from the Carlton Hotel to the quay adjourning the Central Station, where they embarked on one of the B.P.M. launches and proceeded to the Laboratories on the north bank of the Y. They were received by Mr. Caviet, Director of the Laboratory, who gave a short account of the history and growth of the Laboratories. Each member of the party had previously been asked to indicate which section of the Laboratory he was most interested in, and as far as possible the wishes of everybody were observed. In the limited time available for the visit it was impracticable to see more than a small section of these magnificently equipped laboratories in which over 800 scientists are engaged.

The visitors were divided into small groups of five to eight persons, each group having one or two guides, who spared no effort to make the visit of their guests as interesting and informative as possible. The arrangement of the groups and their respective guides was as follows :

Group 1. Special subjects concerning testing and working of oil and its products. Ir. W. L. Brocades Zaalberg.

Group 2. Distillation and extraction. Mr. C. G. Verver.

Group 3. Polymerization and hydrogenation. Mr. J. S. Doting.

Group 4. Physical, routine and research work. Dr. W. R. van Wijk.

Group 5. Application of asphaltic bitumen in road construction and hydraulic engineering. Dr.-Ir. J. Ph. Pfeiffer.

Group 6. Industrial applications of asphaltic bitumen excluding road construction and hydraulic engineering. Ir. W. Slotboom.

Group 7. Testing auxiliary materials used in the petroleum industry. Mr. R. J. Forbes.

Group 8. Organization of the Laboratories and administrative treatment of orders and researches. Ir. J. H. Vermeulen.

At 1 p.m. the visitors were most hospitably entertained by the Directors of the Company in the Conference Hall of the Laboratories, which had been delightfully decorated for the occasion.

Dr. E. R. Redgrove (Member of Council) proposed the toast of Mr. Caviet, and asked him to convey to the Directors of the Bataafsche Petroleum Maatschappij the sincere appreciation of those who had the honour, the privilege and the pleasure of being their guests on this memorable occasion. They were filled with admiration of all that they had seen; the magnitude and the thoroughness of the work carried on at the Amsterdam Laboratories were a living monument to a wonderful organizing power which few, if any, could hope to equal and none could hope to surpass.

In some quarters petroleum was regarded as the root of all evil but, as this was the opinion only of certain politicians, journalists and suchlike people, who knew nothing about the job, it could be disregarded. He thought that when the present page of history was turned over, posterity would realize that petroleum, by providing the world with cheap and rapid transport, was the herald of the Era of International Understanding, the only basis on which lasting peace could be established.

Service of mankind was the highest ideal to which a human being could attain, and Mr. Caviet and his colleagues had given them a striking example of this noble service faithfully performed.

Finally he wished to thank Mr. Caviet, and through him his Directors, for their most generous hospitality; not only the deed but the spirit in which it was offered would always remain a greatly treasured memory.

Following the luncheon three launches were placed at the disposal of the visitors by the B.P.M. The first took a party of about twenty visitors to the works of Werkspoor, where they were received by the Chairman and directors of the Company. An interesting tour was made round the diesel-engine erecting shops, machine ships and forge. At the conclusion of the tour the members of the party were entertained to tea, and brought by motor-coach to their hotels.

The second party visited the works of Messrs. Kromhout, where they were received by Mr. Goedkoop and his co-directors. An equally interesting afternoon was spent in watching the various stages in the manufacture of high-speed C.I. engines. Following tea in the Company's boardroom, the party returned by motor-coach to Amsterdam.

A third launch took back a few visitors who wished to spend the afternoon sight-seeing in Amsterdam.

The visitors left Amsterdam for the Hook of Holland on Monday evening. At The Hague, Mr. Cool and friends were waiting on the station to bid them au revoir. When finally the visitors boarded the S.S. *Amsterdam* for England, it was with feelings of deepest appreciation for the kindness of their Dutch hosts, and recollections of pleasant friendships formed during a week-end which had been all too short.

Ladies' Excursions.

On May 8th, 9th and 11th, a series of extremely interesting excursions in The Hague and district, and in Amsterdam, was arranged for the lady members of the party.

On Friday morning, May 8th, the principal places of historic interest in The Hague were visited by motor-coach. The tour included the Mauritshuis (Royal Art Gallery), the Parliament Buildings (First and Second Chambers of the States-General), the ancient prison of Gevangenpoort, the Royal Palace, the Peace Palace and the Palace of H.R.H. The Princess Juliana. From The Hague the tour was continued to the seaside resort of Scheveningen, and lunch was taken at the Kasteel ond Wassanaar, a beautiful old private mansion converted into a luxury hotel.

Delft was next visited, and its many places of historic interest. The visitors were shown over the celebrated Delft Pottery works, and watched the artists at work painting the designs on the pottery before baking. At the conclusion of the tour, Mrs. Waterman kindly entertained the ladies to tea at her home in Delft.

A further visit was made to the Mauritshuis Museum and Art Gallery in The Hague on Saturday morning.

At Amsterdam on Monday morning, May 11th, a tour by motor-boat was made through the canals and harbours—the most satisfactory method of obtaining a general impression of the city. A walk round the principal shopping centre was followed by luncheon at the Lido Restaurant. The afternoon was spent in visiting the Rijks Museum (Rembrandt Pictures), and the Colonial Museum (exhibition of the sugar, coffee and rubber industries of the Dutch colonies).

The lady members of the I.P.T. party are deeply grateful to the Dutch ladies who acted as their hostesses, and their thanks are due to Mrs. Waterman, Mrs. Cool, Mrs. Sangster and Miss van Panhuys for their generous hospitality and unfailing kindness in making their visit so thoroughly enjoyable.

Visit to Werkspoor, May 11th, 1936.

A party of the members of the Institution paid a visit to the Werkspoor Works in Amsterdam.

The works of Werkspoor is one of the oldest engineering establishments in Holland, as it has now been in existence well over a hundred years.

Although internationally perhaps best known as builders of marine diesel engines, Messrs. Werkspoor specialize in a large variety of work :

stationary diesel engines, steam-engines, pumping machinery, boilers, sugar machinery, locomotives, etc.

They also have a works in Utrecht for the manufacture of rolling stock and structural work. In this latter works the diesel-electric trains for the Netherlands Railways were built.

Messrs. Werkspoor have been among the first to take up the construction of diesel engines, and were the very first to design and build a reversible marine diesel engine for a seagoing vessel—the M.V. *Vulcanus*, to the order of the Anglo-Saxon Petroleum Co. This ship was launched in 1910, and since that time Messrs. Werkspoor have taken a prominent and leading place among the makers of marine diesel engines. Various well-known British firms build Werkspoor engines under licence.

At the time of the visit, several large-sized engines could be viewed in the very spacious and most modernly equipped diesel-erecting shop. In particular a completely finished eight-cylinder supercharged four-cycle engine of 4000 s.h.p., destined for a tanker of the Royal Dutch-Shell Co., attracted the attention of the members.

Mr. G. J. Lugt, who is the designer of this engine, showed the party the various special constructions for which the Werkspoor engine is famous: the piston-dismounting scheme, the very clever reversing mechanism, the simple and effective fuel-pump arrangement, and the under-piston supercharging which is Werskpoor's latest addition to the development of the four-cycle engine.

Messrs. Werkspoor are also licensees of Messrs. Sulzer Brothers for the manufacture of two-cycle engines, several parts of which were going through the shops at the time of visiting. Members were particularly interested in the transportation facilities in the erecting shops, which allow the engines to be placed in the ships, almost without any stripping or dismounting.

Time did not permit an inspection of the general machine shop, but a hurried visit was paid to the forge, where some large crankshafts, rudder-posts, etc., were being forged.

There was also occasion to see a high-pressure oil pump for the oil-refinery, which is being erected at Pernis, near Rotterdam.

In other workshops the boilers and turbine-parts of the 56,000-H.P. machinery for a flotilla leader, under construction for the Dutch Government, were viewed, and finally attention was given to a Maybach-Diesel engine on the test-bench, to which a Standard Sunbury Cathode Ray Indicator was fitted.

The visit ended in assembling the members at tea in the Directors' room. Mr. A. C. Hartley expressed the thanks of the Institution to Messrs. Werkspoor for their courtesy of allowing the Institution to visit their interesting works, and Mr. Maas Geesteranus, managing director, responded.

THE CORRELATION OF TESTS ON THE IGNITION QUALITY OF DIESEL FUELS, CARRIED OUT AT DELFT AND SUNBURY.*

By Ir. G. D. Boerlage, Ir. J. J. Broeze, L. J. Le Mesurier and R. Stansfield.

Introduction.

The correlation tests to be described on the ignition quality of diesel fuel are the outcome of differences found in the two laboratories involved regarding the rating in terms of cetene number of some commercially used fuels.

The object of using suitable reference fuels is, of course, to eliminate engine factors so as to obtain identical results. The differences actually found during the early tests seemed to support the views of the pessimists who looked on ignition quality and cetene numbers merely as new sources of trouble. Now that a great deal of work has been done, it is believed that on hearing the results it will be agreed that there is no room for such pessimism.

For the major part of the work not only the order of merit of a series of fuels containing straight-run petroleum fuels has scarcely varied when rated in eight different engines by different methods, but also, except with one method of testing, the rating against the primary reference fuels cetene and α-methylnaphthaline has resulted in very nearly identical cetene numbers; 100 per cent. cracked and doped fuels tend to give anomalies.

In general, therefore, the results, especially those on the basis of ignition delay measurements, have been gratifying, although it is admitted that both laboratories concerned were rather relieved when the first sets of data had been compared!

A few words to illustrate what is meant by rating on the basis of ignition delay may be in place here. If a time-pressure diagram of an oil engine is given together with an injection diagram, the injection starting at A and the pressure rise at B (Fig. 1), then A–B is the ignition delay. A curve can be drawn connecting the delays for a series of reference fuels ranging from 100 per cent. cetene to 100 per cent. α-methylnaphthaline; this shows that the delay increases at first slowly and then more rapidly with decreasing cetene number. The determination of the cetene number of a fuel is merely the result of plotting its delay in the chart shown and reading off the cetene number at the intersection of this value with the reference curve.

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* Paper presented for discussion at a meeting of The Institution of Petroleum Technologists and The Koninklijk Instituut van Ingenieurs at The Hague, 8th May, 1936.

It is seen how with increasing cetene number the delays are closer together; actually in many cases fuels with cetene numbers of over 60 have such minute differences in delay that relatively large experimental errors may result. This is rather due to the nature of the scale used, which is rectilinear when it should be more nearly exponential. Whereas,

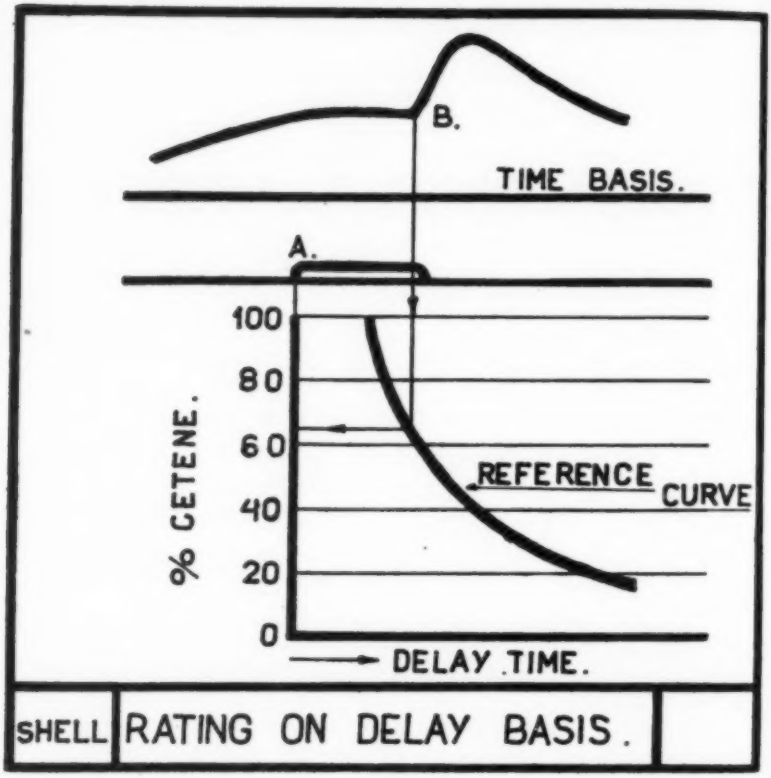


FIG. 1.

therefore, in petrol-knock rating the importance of an octane point rises towards the upper end of the scale, in ignition-quality rating the importance of a cetene point falls. Added to this is the fact that there is no definite urge towards high cetene numbers, as there is towards high octane numbers. Practically, therefore, differences between such figures as 60 and 65, or between 70 and 80, are negligible, and in general a tolerance of plus or minus 5 per cent. of the cetene number can be allowed in practice.

After a first series of fuels have been tested purely as a means of satisfy-

ing ourselves regarding the origin of the early differences referred to above, it was thought that these tests could be useful to the committee of your Institution which deals with ignition quality. It was agreed, therefore, to carry on the tests on behalf of this committee in anticipation of co-operation from other laboratories. A new series of fuels, amongst which were the cracked and doped fuels mentioned before, was decided on; again quite good correlation was found.

There still remained one difficulty—the behaviour of peanut oil—for amongst the new oils tested this one seemed to spoil the picture completely, its cetene number taken on different engines varying from 35 to 60! It is inopportune in the present paper to discuss this discrepancy in detail, but reference is made to an hypothesis concerning oil-spray ignition, which was described in a very recent paper to the American Chemical Society. For the present it may suffice to point to the fact that for all normal diesel fuels and normal engine conditions the correlation tests between the two laboratories were quite satisfactory.

The following tables (Tables I and I*a*) give the more important physical constants of the fuels examined.

TABLE I.

Constants of Fuels used for Correlation Tests.

Fuel.	Sp. Gr. 60° F.	A.S.T.M. Distillation Temperatures.				Visc. at 100° F. c.s.	Aniline Pt. °C.
		I.B.P.	10%.	50%.	90%.		
Methyl naphthalene . A.	1·025	237	238½	239	239	2·23	below −19
Cetene . . . . C.	0·785	274	276	276½	277	2·76	71·8
Stght.-run Gas Oil (paraffinous) . . . P.	0·847	213	245	285	342	3·88	71·2
Aromatic Extract . . Q.	0·874	172	197	213	240	1·47	1·0
Stght.-run Gas Oil (paraffinous) . . . R.	0·837	221	248	276	322	3·50	73·4
Aromatic Extract . . S.	0·934	213	228	248	286	2·31	approx. −10
Stght.-run Gas Oil (mixed base) . . . . T.	0·862	215	255	291	354	4·74	68·2
Stght.-run Gas Oil (naphthenic) . . . U.	0·862	192	231	279	342	3·98	65·4
Stght.-run Gas Oil (asphaltic) . . . W.	0·854	190	213	245	308	2·61	55·2
Gas Oil (shale origin) . K.	0·836	205	239	282	330	3·3	62·2
Stght.-run Gas Oil (asphaltic) . . . M.	0·859	198	221	251	318	2·9	54·8
Cracked Gas Oil (paraffinous) . . . N.	0·862	210	218	236	267	2·2	41·0
Cracked Gas Oil (asphaltic) O.	0·861	203	225	236	275	2·2	42·8
Nut Oil (Arachis) . . J.	0·917	182	300	315*	—	41	16·0

* (Decomposition prevented further distillation.)

In addition to the above, fuel M. was treated with various percentages of ethyl nitrate and also with acetone peroxide to determine the effect of doped fuels.

TABLE Ia.

Arachis Oil (J).

Iodine number 95·92 (average of 95·98 and 95·85)
Saponification number 186·4 (,, ,, 185·1 and 187·6)
Viscosity Engler 50° C. 3·76 (calculated from 27·4 cs.)

Fuel.	Spec. Grav. 15/15° C.	* Index of Refraction at 15° C. Determined with the Abbé Refractometer.
J	0·9164	1·4728
K	0·8364	1·4705
M	0·8599	1·4774
N	0·8633	1·4861
O	0·8619	1·4798
P	0·8470	1·4726
Q	0·8742	1·4964
R	0·8372	1·4676
S	0·9333	1·5384
T	0·8625	1·4806
U	0·8629	1·4778
V	0·8542	1·4740

* Average of two observers. Spread ± 0·0002.

THE DELFT TESTS.

The following are the engines and test conditions used for the Delft experiments :—

TABLE II.

Engines and Conditions.

Engine.	Thomassen.	Gardner.				C.F.R.			Ricardo.		
Type	W_2C.	1 L.W.				" Delft "			16–1 W.		
No. of Cylinder	1	1				1			1		
Horizontal or Vertical	Horizontal	Vertical				Vertical			Vertical		
Cycle	4-Stroke	4-Stroke				4-Stroke			4-Stroke		
Injection	Direct	Direct				Turbulent chamber of variable volume			In " whirlpool " chamber		
Injection Pressure	100 atm.	175 atm.				100 atm.			100 atm.		
Bore Stroke	210 × 370 mm.	108 × 152·4 mm.				83 × 114 mm.			120 × 140 mm.		
Volume (litre)	12·8	1·4				0·618			1·58		
Compression Ratio	(Compression pressure, 30·5 atm.)	1 : 13				1 : 20·7		1 : 19	1 : 17·5		
R.P.M.	275	1500			800	900		900	1300		
B.H.P.	6·05	15	12	15·75	1·6	2·5	0·9	2·3	2·6	5·6	13·5
B.M.E.P. in kg./cm.^{2}	1·55	6·43	5·15	6·75	1·29	4·0	1·45	2·64	1·14	2·45	5·9
Cooling Water Outlet, °C.	50	60	60	60	40	100	100	100	50	60	60

All tests were made by direct measurement of the ignition delay by means of an indicator. With regard to previous methods of determining the delay, we may refer to a paper in the *S.A.E. Journal*, July 1932.

The Thomassen engine equipped with a normal Maihak piston indicator No. 3 is the routine testing engine for cetene-number determination. The

indicator draws an out-of-phase pressure diagram on a sheet of specially prepared paper by means of a copper pin. The indicator is fitted in such a way that the spray-valve lift diagram can be taken on the same indicator paper.

On the high-speed engines an optical indicator was used, indicating by moving a light spot on a sheet of transparent paper. The principle of working of this indicator is based on the deflection of a light beam by a

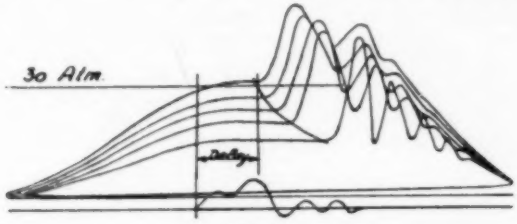


FIG 2.

METHOD OF MEASURING THE IGNITION LAG WITH MAIHAK INDICATOR ON THOMASSEN ENGINE.

prism fitted eccentrically on a diaphragm; the diaphragm being the pressure element. With this indicator it was also possible to take a needle-valve lift diagram (a description of this indicator is given in the July issue of the *Automobile Engineer*, 1935). According to the results obtained on the different engines, it appears that the accuracy obtainable with this indicator is amply sufficient for the tests made.

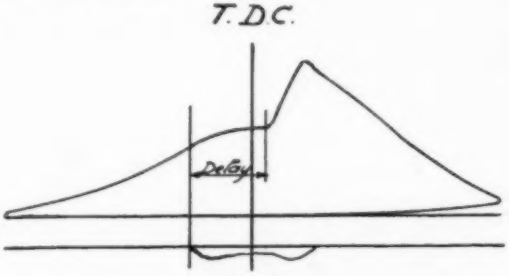


FIG. 3.

METHOD OF MEASURING THE IGNITION LAG WITH OPTICAL INDICATOR.

A complete diagram as taken on the Thomassen engine with the Maihak indicator consists of a needle-valve diagram and two out-of-phase pressure diagrams taken with increasing throttle-valve position. The delay had been determined by measuring the distance between the moment of injection and the intersection of a 30-atm. line with a curve drawn through the point of beginning of rapid pressure rise (compare Fig. 2).

The delays with the optical indicator could be obtained by marking the beginning of injection and rapid pressure rise. An example of such a diagram is given in Fig. 3.

TABLE

Engine.		SUNBURY.									Spread. Starting Test.	
		A.E.C.	Gardner.				C.F.R.					
		2 B.H.P. 750.	2 B.H.P. 600.	7½. 1000.	12. 1500.	Start. Test.	1·5. 900. 14 : 1.	1·5. 900. 15 : 1.	1·5. 900. 17·2:1.	Crit. C.R.	Incl.	Excl.
Stght.-run Gas Oil (paraffinous)	P.	61	60	61	62	71	59	59	59	60	12	3
Aromatic Extract	Q.	—	24	22	23	—	—	—	—	—	2	2
Stght.-run Gas Oil (paraffinous)	R.	64	60	63	62	74	61	63	60	62	14	4
Aromatic Extract	S.	—	23	20	22	—	—	—	—	—	3	3
Stght.-run Gas Oil (mixed base)	T.	58	56	56	57	66	53	55	52	55	14	6
Stght.-run Gas Oil (naphthenic)	U.	53	50	51	51	59	54	51	51	51	9	4
Stght.-run Gas Oil (asphaltic)	W.	45	42	42	42	49	41	41	41	42	8	4
Shale Origin	K.	—	66	69	68	78	65	61	64	63	17	8
Stght.-run Gas Oil (asphaltic)	M.	—	46	45	43	43	45	45	45	43	3	3
M + 1% Ethyl Nitrate (by vol.)		—	47	53	57	46	51	50	49	50	11	10
M + 1% Ethyl Nitrate (by vol.)		—	52	62	68	55	56	58	55	55	16	16
M + 2% Ethyl Nitrate (by vol.)		—	57	70	78	64	62	67	61	58	21	21
M + 0·4% Acetyl Peroxide (by wt.)		—	51	57	59	52	52	53	55	55	8	8
M + 0·8% Acetyl Peroxide (by wt.)		—	54	63	65	61	58	58	60	58	11	11
M + 1% Acetyl Peroxide (by wt.)		—	62	70	78	75	68	71	64	64	16	16
Cracked Gas Oil (paraffinous)	N.	—	40	49	52	50	47	45	47	43	12	12
Cracked Gas Oil (asphaltic)	O.	—	40	38	41	35	—	36	40	39	6	5
Arachis	J.	—	43	48	66	42	—	38	34	39	32	32

III.

Delft.												
Thomassen.	Gardner.			C.F.R.			Ricardo.			Spread.	Total Spread.	Total Spread (Excl. Starting Tests).
6 B.H.P. 275.	1·6. 800.	12. 1500.	15. 1500.	2·5. 900. 20·7:1.	0·9. 900. 20·7:1.	2·3. 900. 18 : 1.	2·6. 1300.	5·6. 1300.	13·5. 1300.			
56	61	61	58	59	57	—	59	—	—	5	15	6
24	—	—	23	—	—	—	—	—	—	1	2	2
58	63	62	58	60	60	—	62	—	—	5	16	6
—	—	—	—	—	—	—	—	—	—	—	3	3
52	57	56	56	53	53	—	56	—	—	5	14	6
49	52	53	51	49	50	—	51	—	—	4	10	5
43	45	44	43	42	39	—	45	—	—	6	10	6
63	—	—	66	—	—	68	—	68	66	5	17	8
42	—	—	44	—	—	46	—	47	47	5	5	5
49	—	—	56	—	—	54	—	57	57	8	11	10
51	—	—	61	—	—	58	—	64	63	13	17	17
58	—	—	70	—	—	65	—	72	72	14	21	21
49	—	—	55	—	—	54	—	57	57	8	10	10
55	—	—	62	—	—	62	—	64	64	9	11	11
64	—	—	73	—	—	73	—	74	73	10	16	16
46	—	—	52	—	—	49	—	53	52	7	13	13
37	—	—	40	—	—	37	—	42	41	5	7	6
34	—	—	59	—	—	47	—	40	41	25	32	32

The mean value of the delays obtained from four diagrams of every fue has been determined. The cetene numbers of the fuels have then been found by comparing the mean delays with those of cetene/α-methylnaphthaline blends, determined during the same test run.

All tests have been repeated once or more, and in some cases by different observers.

The Delft test results as shown in the right-hand side of Table III are the mean values of the cetene numbers obtained from the different tests; the left-hand part of this table gives the results from the Sunbury laboratory. On the right of each section are given the ranges over which the cetene numbers spread in both laboratories, and on the extreme right the total range. It will be seen that the major spreading is caused by : (*a*) the doped fuels, (*b*) the peanut oil, and (*c*) the Gardner starting test.

The Sunbury Tests.

Early tests for ignition quality at Sunbury began about six years ago, and for some time the Farnborough Indicator was used for determining the delay angle. An accuracy of about ½ a degree of crank angle was obtainable by averaging results from two or three diagrams and provided the operator was sufficiently experienced.

Later the Strobophonometer was developed to measure relative noise effects, and gave values in very good agreement with the delay measurements unless very low ignition quality fuels were tested. In such cases the noise was found to fall, but the fuel consumption rose appreciably above normal.

For the last eighteen months use has been made of a cathode-ray oscillograph indicator developed in the laboratory (a description of this indicator is given in *The Engineer*, December 13th, 20th and 27th, 1935).

This apparatus makes use of an electro-magnetic system of indicating units, and can be applied to obtain either diagrams of rates of change of pressure (or diagrams of spray valve velocity) or normal pressure and valve-lift diagrams at will by simple switching. The most suitable diagrams for delay angle measurements are the former because, as first differentials of the usual diagrams, they show much more precisely the exact time at which any change of curvature, such as that at the beginning of combustion, starts.

This is illustrated by Figs. 4 and 5, which are traced from C.F.R. diesel engine diagrams.

Fig. 4 shows the usual cylinder pressure and spray valve-lift diagrams, the delay angle being about seven degrees. It will be noticed that the beginning of combustion is somewhat difficult to ascertain with certainty, on account of the easy curvature between the compression and combustion lines. Fig. 5 shows the diagram of rate of change of pressure as a full-line and the velocity diagram of spray valve-lift as a dotted line.

The precise opening point of the valve and a much more accurate estimation of the beginning of combustion are obtainable from these records, and repeatability to better than one quarter of a degree of crank angle is simple even for an unskilled observer.

The Gardner starting test was described in a paper presented at the

World Petroleum Congress in 1933, and although results by this method do not always agree in terms of primary standards with results by other methods, the technique may be valuable in connection with starting as distinct from running quality measurement.

When examining the test fuels on the C.F.R. diesel engine, tests were made at three different compression ratios, and also by a method which involved reducing the compression pressure while the engine was running under load until misfiring took place. The latter method is described as a critical compression ratio test, but should not be confused with the critical compression ratio test used in America, in which the ratio is slowly raised on a motored engine until the test fuel just fires at the first injection. Table IV summarizes the engines used and the test conditions.

Tests were also made on some of the fuels in a Robey engine running at 275 r.p.m. (9½-in. bore 17-in. stroke) and developing 24 b.h.p. The

TABLE IV.

Engine.	Type.	Test Series.	B.H.P.	R.P.M.	Jacket Temp. °C.	Inlet Air, °C.	Compression.		Remarks.
							Press. kg./sq. cm.	Ratio.	
A.E.C.	Comet air cell	1	3	750	70	atmos.	—	—	—
Gardner L.W.	Direct-injection open chamber	2	2	600	50	25	—	—	—
		3	7½	1000	75	50	—	—	—
		4	12	1500	75	50	—	—	—
		5	—	300	50	30	—	—	Starting test with critical throttling.
C.F.R. diesel	Air cell	6	1½	900	100	atmos.	29·5	14 : 1	—
		7	1½	900	100	atmos.	33·1	15 : 1	—
		8	1½	900	100	atmos.	40·1	17·2 : 1	—
		9	1½	900	100	atmos.	—	—	Reduction of compression to limit of steady firing.

results in terms of cetene numbers differed from the average results of all the other engines by amounts up to 5 cetene numbers, and agreed best with values from the C.F.R. engine, but as only one series of readings could be taken from this engine (on account of the large amount of fuel needed and also because the governor tended to hunt badly and give erratic spray-valve operation), there is doubt regarding the accuracy of the figures, and they are not reported. They show tendencies very similar to the Thomassen engine mentioned in connection with the Delft tests.

The method of test in all cases in which delay angle measurements were used as the criterion of ignition quality was as follows :—

The engine was run until conditions were steady, and then blends of two fuels, one of high-ignition quality (*P*) and one of low-ignition quality (*Q*) adopted as secondary standards, were examined, and a curve was prepared showing the relation between the delay angles measured from the indicator diagrams and the percentage of *Q* in each of the blends of these secondary standards. The remaining fuels in the series were then examined for delay angle, and the plotted curve used to determine the blend of secondary standards which gave the same delay angle. This procedure was repeated

for several of the fuels on three separate days, and by different observers, so that the probable experimental error could be ascertained.

In order to convert results to cetene numbers, a further series of tests was made to compare the secondary standard blends with blends of cetene and α-methylnaphthalene, and a correlation curve between cetene blends and secondary blends plotted. This curve had, of course, to be determined for each engine, and also for each different set of operating conditions.

The following table (Table V) gives the results in terms of blends of secondary standards, *P* and *Q*, the figures being the percentage of fuel *Q* (low quality) in fuel *P* having the same delay angle as the sample, or, in the case of the Gardner starting test and the C.F.R. critical compression ratio test, the blends matching the sample at the limiting conditions for firing.

Certain of the fuels could not be tested in terms of secondaries because the quality of fuel *P* was not high enough, but there would be no difficulty in producing a similar type of secondary specially for test use higher in quality and suitable for rating any fuel likely to be of commercial importance.

TABLE V.

Test Fuel.	Series.									Range of *P* in *Q*.	Approx. Cetene Range.
	1.	2.	3.	4.	5.	6.	7.	8.	9.		
T. . .	13	10	14	13	11	15	12	18	13	8	3·2
U. . .	27	28	27	28	27	13	22	21	24	15	6
W. . .	45	49	49	51	44	50	50	50	51	7	2·8
M. . .	—	39	41	49	54	37	37	37	46	15	6
½% e.n. .	—	35	21	12	49	20	24	26	26	37	14·8
1% e.n. .	—	21	0	—	34	6	2	10	40	35	14
0·4% a.p. .	—	25	11	7	40	18	16	10	14	33	13·2
0·8% a.p. .	—	16	—	—	23	2	2	—	5	> 21	> 8·4
N. . .	—	38	31	24	42	33	37	31	46	18	7·2
O. . .	—	56	59	54	65	—	60	51	58	11	4·4
J. . .	—	48	34	< 0	55	—	55	67	57	> 67	> 26·8

DISCUSSION AND SUMMARY.

During the period of the tests which have been described, correlation work has also been making progress in the U.S.A., and, while the results have not yet been made public, it is understood that quite a satisfactory measure of agreement has been obtained between various co-operating laboratories. In practically all cases the C.F.R. diesel engine has been used in conjunction with the modified bouncing-pin, and opinion has been expressed that although the results are in good agreement, the bouncing-pin is not an entirely suitable measuring instrument.

Taking into account these American tests as well as those made at Delft and Sunbury, it is clear that correlation between laboratories for diesel fuel rating should not be nearly as difficult to obtain for normal fuels as it has been for octane-number determinations of gasolines, tests made under running conditions showing a surprisingly good agreement even when many engine types are used.

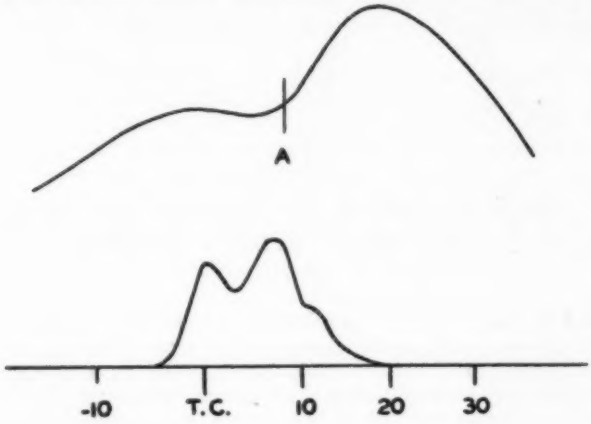
Three major points require decision. They are :—

(*a*) Is the bouncing-pin necessarily an imperfect and unsuitable measuring instrument for diesel knock ?

(*b*) Is there any need for a special test engine and a strictly defined test technique and, if so, what type of engine should be used ?

(*c*) Are either of the proposed primary standards (cetene for the Delft/Sunbury tests and cetane for the U.S.A. tests, each used with α-methylnaphthalene) free from objections and, if not, can anything be done to overcome these objections ?

Schweitzer and Hetzel have dealt in some detail with the defects of the bouncing-pin (S.A.E. Annual Meeting, 1936), and have used a simple arrange-

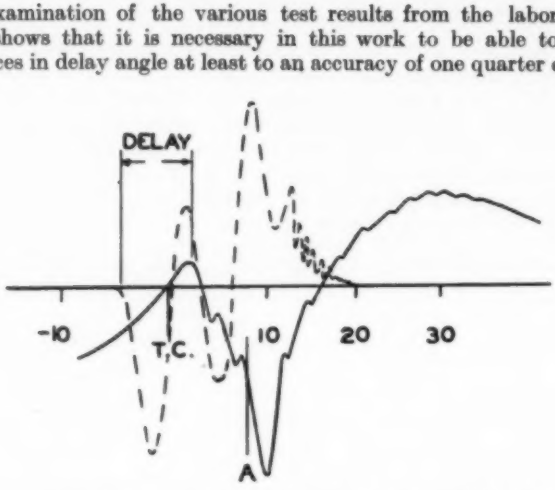


CYLINDER PRESSURE AND VALVE LIFT DIAGRAMS.

FIG. 4.

ment which shows by flashes of a neon tube the time at which the rate of pressure rise and the velocity of the spray valve reach certain critical values. Suitable operating points are marked "*a*" on Figs. 4 and 5. This method has the advantage that it eliminates the friction of the bouncing-pin, which is probably the greatest single factor contributing to its uncertainty; but there is still a chance of error arising between fuels which burn at different rates after ignition begins. The nut oil tested by the Delft and Sunbury laboratories would be rated in an entirely misleading manner by this instrument in many cases, and it seems likely that both very low and very high viscosity fuels might also be altered from true ratings by its use. It would also be affected in a way not obvious to the operator by any chance erratic working of the spray valve, particularly by a small primary lift not sufficient to induce a good fuel spray.

An examination of the various test results from the laboratory test sheets shows that it is necessary in this work to be able to ascertain differences in delay angle at least to an accuracy of one quarter of a degree



RATE OF CHANGE OF CYLINDER PRESSURE AND VALVE VELOCITY DIAGRAMS.

FIG. 5.

of crank angle for good reproducibility, and twice this accuracy is desirable for averaged values. For this purpose the rate of change of pressure diagram and the spray-valve velocity diagram seem to be ideal, and there should be no difficulty in making a simple and cheap cathode-ray oscillograph indicator with only one stage of amplification specially for this duty if there is a reasonable demand for it. One very great advantage of such an instrument over the bouncing-pin, and even over the apparatus developed by Schweitzer and Hetzel, is that no setting and adjusting instructions are required to obtain repeatability, since the indicator diagram shows the actual events which occur and does not require to be set to any special conditions based on trial-and-error experience. It also has the advantage that any stray erratic working of the fuel system is at once revealed.

As regards the need for a special test engine, it appears from the Delft/Sunbury figures for all normal diesel fuels, including cracked fuel, that the ratings from running tests, as distinct from starting tests, are little affected by either the engine or the running conditions adopted, but that the three service type high-speed engines used, viz. the Gardner, the A.E.C. and the Ricardo, agree better between themselves than they agree with the C.F.R. engine under any running conditions of the latter.

Both laboratories agree that the reproducibility of ratings on the Gardner engine is at least as good as that of any of the other engines, and that its indicator diagrams are the easiest to read.

When the starting tests on the Gardner engine are considered, it is seen that the ratings of normal straight-run and cracked fuels agree well with

the running ratings only when determined in terms of the secondary standards *P* and *Q*, and that the agreement is poor when the actual cetene numbers are compared. The inference is that any type of engine and test conditions are suitable for fuel testing when normal types of fuel are being examined and secondary standards of mineral origin employed. Another inference is that, for preference, when using primary standards, abnormal test conditions should not be used.

Unfortunately, cetene (and there is evidence that the remark applies also to cetane) is affected more by both change of engine and change of operating conditions than are the secondary reference fuels.

Since the ratings of fuels for high-speed engines are much more important than those of fuels for slow-speed engines, it may be asked whether an engine such as the Gardner is not more suitable as the standard type than the C.F.R., which, according to the tests reported, does not give such typical results.

As regards practical testing, definite progress might be made were a supply of reference fuels of mineral origin available. Using these, anyone having a single-cylinder service type of high-speed engine could, with a suitable indicator, make ignition-quality tests by direct comparison of delay angles with the assurance that the engine type will not make any important difference to the ratings as long as only normal fuels, including cracked products and shale oils, are being examined. A scale of 0 to 10 numbers of ignition quality, reported to the nearest half-number, and equivalent to a cetene number range from about 25 to 75, would meet requirements. If it is felt to be desirable to have a conversion curve from which the ignition numbers obtained in this manner could be converted to a scale of cetene or cetane numbers, then three or four favourably situated laboratories might arrange for periodical calibrations of the secondaries in a selected make of test engine under standardized test conditions. The primaries would be used only for such calibrations, and would not be required for general testing.

Emphasis has, so far, been placed on the fact that agreement is good only for normal fuels. When the results for the doped fuels and the nut oil are studied, an apparently difficult situation arises. It will be seen that both the doped blends and the vegetable oil are far more affected by change of engine, and even by change of running conditions in a given engine, becoming noticeably less efficient with light-load cool operation just when dopes are most needed to reduce light-load knock.

Two courses appear to be open. First, such special fuels might be tested in an engine and under running conditions selected to give a rating which is about the average of a large number of ratings, each determined in service-type engines under many possible running conditions. Such averaging could be an exceedingly difficult matter. Alternatively, and preferably, it may be agreed that such engine-sensitive fuels cannot, from their nature, be rated satisfactorily in any test engine by average values, but that they must inevitably be rated always in the actual engine and under the running conditions under which they will be used.

No tests have been made in this series on oils derived from coal. This is because it is difficult yet to obtain any such material of reasonably high-ignition quality which may be considered a typical product.

Blends of coal with paraffinous oils similar to *P* and *R* have been dis-

tributed in small quantities, and their characteristics as regards sensitivity to change of engine and engine conditions is small. Such data as are available from low-ignition-quality unblended coal oil suggest that it behaves very like the low-quality primary or secondary reference fuels. There is thus little reason to expect that coal oils cannot be tested in the same manner as petroleum oils.

If coal oils with added dopes become of interest, it is inevitable that they must be tested in the engine in which they have to be used and under the running conditions for which the use of dope is most important.

Summarizing, the proposed technique for testing diesel fuels for ignition quality becomes a combination of laboratory chemical test and a running test. The laboratory test will be able to determine whether the fuel is of mineral origin; if it is not, or if it is obviously doped, no rating in a single engine can be expected to give more than an approximate idea of how it will behave in a different engine. If the fuel is a normal straight-run mineral oil, a shale oil or a cracked product, then it can be rated in terms of suitable mineral secondaries in almost any type of diesel engine without serious risk that large differences will be found between one engine and another.

Should a primary reference scale be desired, then a standard engine and standard running conditions must be adopted for calibration of the secondaries in terms of the primaries; but it is desirable that this engine and the test procedure adopted should bear a close relation to average commercial practice.

There does not seem to be any reason why secondary reference fuels of mineral origin, and covering a suitable range of ignition quality, should not be made generally available at an early date and, once this is accomplished, the less important question of primaries and special test engines can be dealt with as further experience is obtained. There is, of course, no serious difficulty in reproducing standardized diesel reference fuels, and the general use of pure hydrocarbon primaries so often urged in the early days of gasoline testing is not at all important.

DIESEL-ELECTRIC TRACTION ON THE NETHERLANDS RAILWAYS.

By Ir. W. Hupkes.*

Due to the rapid increase in road transport, the travelling public has grown to appreciate the advantages of frequent services, and would no longer tolerate the infrequent services, irregularly divided over the day, as they were offered by the railway companies until a short time ago.

To meet these demands the railways have to give frequent and fast services regularly spread over the day, *e.g.* hourly or half-hourly services.

To run these services with steam traction would be difficult and costly.

The most attractive form for such a service, both for the public and for the railway companies, is electrification. This is, however, only economical on lines with a great volume of regular passenger traffic, due to the high costs of the overhead trolley wire and the substations. For lines for which electrification cannot be considered the internal-combustion motor makes a good solution possible.

In view of these considerations the Dutch Railways decided in favour of diesel-electric trains and to run hourly services on the lines marked on the accompanying map (Fig. 1), which gives also the lines on which electric trains are operated.

The diesel-electric trains had to meet the following demands: seating accommodation had to be provided for 160 passengers in one unit in second and third class in the ratio of $\pm$ 1 : 3; two units coupled together had to be driven by one man; the coupling and uncoupling of two units had to be effected in a very short time and automatically when possible; maximum speed 140 km.p.h. (87 m.p.h.); rapid acceleration was necessary (up to a speed of 100 km./h. (62 m.p.h.), the mean starting acceleration is 0·185 m./sec.^{2} (0·59 ft./sec.^{2})); provision had to be made for the cars when not in service (also in winter-time) to be left in the open air, no running-sheds being available.

On these lines a design was worked out which resulted in the triple-articulated diesel-electric trains as shown in Fig. 2; forty of these trains were purchased.

Of these trains thirty-five are each fitted with two Maybach engines (twenty of which are built under licence by Werkspoor, of Amsterdam); with an electrical equipment, designed by Brown Boveri Cie. (Switzerland) and built partly by this firm and partly by the Dutch firm Heemaf (Hengelo); five are equipped each with two Ganz engines supplied by the Dutch firm Stork Bros. (Hengelo), the electrical transmission being manufactured on Westinghouse principles by the Dutch firm Smit (Slikkerveer). The coaches are all built in Holland by the firms Werkspoor, of Amsterdam

* Paper presented for discussion at a meeting of The Institution of Petroleum Technologists and The Koninklijk Instituut van Ingenieurs at The Hague, 9th May, 1936.

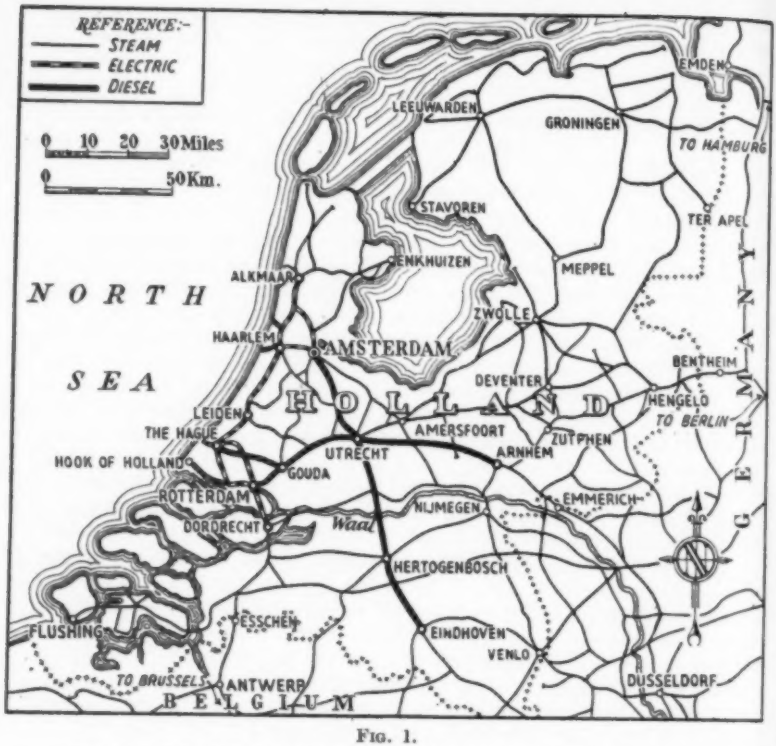


FIG. 1.

MAP OF NETHERLANDS RAILWAYS, SHOWING LINES OPERATED BY DIESEL TRACTION.

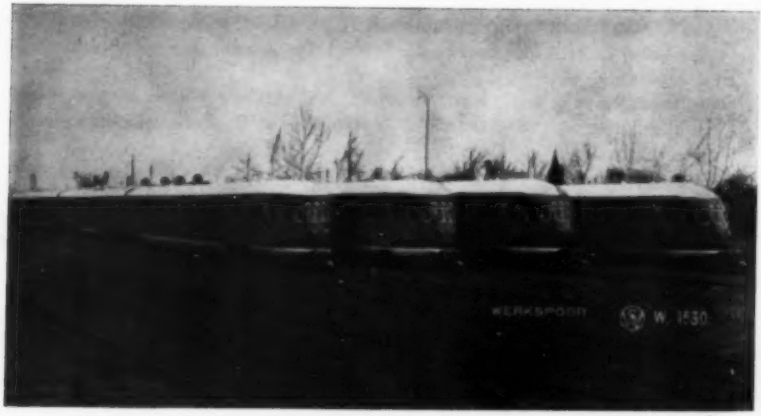


FIG. 2.

(twenty-five Maybach trains), Beynes, of Haarlem (ten Maybach trains) and Allan, of Rotterdam (five Ganz trains).

General Arrangement.

The coach comprises two two-axle carrying bogies at the ends, two three-axle driving bogies between (the end axles of each being driven by a nose-suspended electric motor), and three car bodies. The axle-loads in running order, but without passengers, and in running order with full load are given in Fig. 3.

The weight of the end cars without bogies is about 15 metric tons, that of the centre car about 37 metric tons. The whole unit measures 62,100 metres (203 ft. 9 in.) in overall length.

A vestibule connection is provided between each two cars. A driving-cab has been fitted at each end.

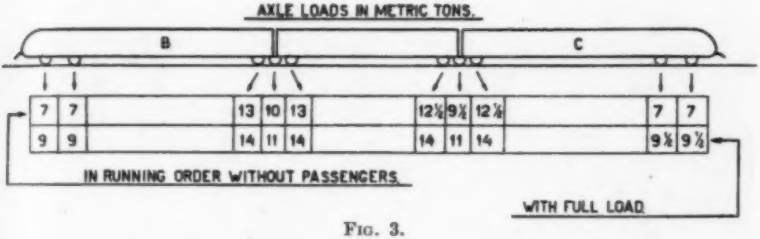

AXLE LOADS IN METRIC TONS.
B
C
7 7 13 10 13 12½ 9¾ 12½ 7 7
9 9 14 11 14 14 11 14 9¾ 9¾
IN RUNNING ORDER WITHOUT PASSENGERS.
WITH FULL LOAD

Fig. 3.

To get a low figure for the train resistance the car is kept as light as possible, is streamlined and has roller bearings on all axles.

With a view to saving weight, the carriage bodies are built up of light sections electrically welded together, and light metals are used for all such parts as doors, parcel nets, reservoirs and air ducts; in one train-unit all the light metal parts together have a weight of 3 tons.

To determine the best aero-dynamical shape, wind-tunnel experiments were carried out at the works of the Zeppelin Airship Company, Friedrichshafen; resistance and pressure measurements were made. In Fig. 4 the model of the train (scale 1 : 25) is shown standing in the wind-tunnel. To get the air-streaming conditions at the underside of the car-model as similar as possible to those in practice, an endless rubber band, shaped in the form of the track with rails and sleepers, was fitted under the model, which band was moved in every test at a speed equal to that of the air-stream in the tunnel.

To enable the cars to be left in the open air at any time when not in service, there is provided a boiler with a thermostatically controlled oil-burner in the cooling-water circuit of each diesel motor, by which, in combination with a little auxiliary circulating pump, the water temperature is kept automatically above 60° C.; this provides the additional advantage that the engines are always warm when started. More particulars are given later.

Bogie and Car Details.

Maximum strength with maximum saving of weight was the key-note of the design of both bogies and cars.

The bogies are of normal so-called American pattern, steel made and all welded. The axles are hollow, with special disc type wheels forced on. S.K.F. roller-bearing axle-boxes are used for all axles. The weight of one axle with wheels is $\pm$ 650 kg. (1430 lb.), whilst the weight of a normal axle with wheels is as high as 1200 kg. (2430 lb.).

The body of each car is constructed as a tube with flat sides, bottom and well-arched roof, the structural material being steel; the whole is built up

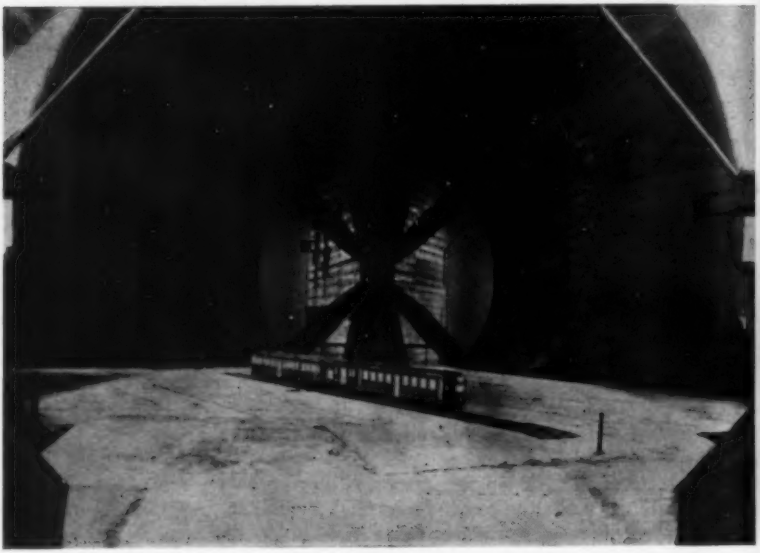


Fig. 4.
TRAIN MODEL IN WIND TUNNEL.

by electric welding. The greater part of the longitudinal framing, the roof carlines, the side posts and transverse connections are made from tubular elements of rectangular cross-section. For the doors, the luggage-racks and end-frames, reservoirs and air ducts, aluminium alloys are used.

Seats are provided for forty-eight second-class and 112 third-class passengers in smoking and non-smoking compartments, the second class occupying one end-car, the third class the other end-car, and three compartments in the centre car, the latter having accommodation for two guards, additional lavatory accommodation for second- and third-class passengers, a luggage compartment and the engine-room.

The second-class seats are upholstered in plush, those of the third class are of latex rubber covered with artificial leather. The lower portion of

the windows is fixed, the upper portions are in the form of sliding lights. Electric lighting is provided.

Motive Power.

In all units the whole power-plant, comprising two engines, two direct-current main generators and the switching apparatus, is installed in the engine-room in the centre car. Each engine with its generator (the latter being coupled to the former by a flexible coupling) are mounted on a frame (Fig. 5), which is supported by the underframe of the car body through

Fig. 5.

the intermediary of four rubber blocks; the construction of these blocks is such that no steel parts are in contact with each other. The two engine-generator sets of one train are in every respect independent; each engine has its own cooling-water system, and no electrical connection exists between the two generators. The train may be driven by either of the two sets alone, the other engine being stopped; lighting, heating and ventilating are the same as when both sets are in service.

The Maybach motor (see the sections in Fig. 6) is a twelve-cylinder four-stroke V engine of the direct-injection type, developing 410 metric h.p. at 1400 r.p.m., cylinder diameter 5·91 in., and stroke 7·9 in. The pistons are of a cast aluminium alloy and carry six pressure rings. The cylinder-heads are not detachable; each head is cast integral with its cylinder, and contains one inlet and one exhaust valve, controlled by rockers from a

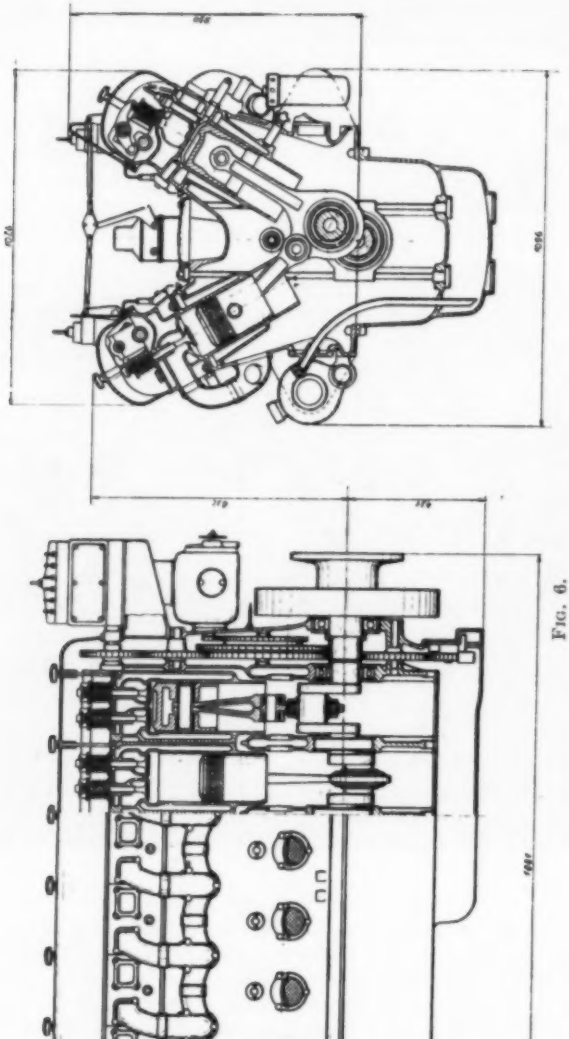


FIG. 6.

camshaft, located on the upper side of each cylinder row. The six-throw crankshaft is supported in seven roller bearings. The big-end bearings of the main connecting-rods of one bank are also roller bearings, the piston rods of the other bank are each linked to the opposite one of the main connecting-rods referred to. The crankcase is of cast aluminium alloy. Fuel is injected by two Deckel pumps. A pressure-lubrication system is incorporated. A special cooler for the lubricating oil could be dispensed with, due to the fact that the air for combustion is drawn into the cylinders through the crankcase, which effects a thorough cooling of both the moving parts and the lubricating oil.

The weight of the motor is about 2030 kg. (4476 lb.). The fuel consumption at the most economical load is about 185 grams per metric h.p./hr.

The motor is provided with a governor, which regulates the delivery of the fuel pumps by means of a servo-motor piston, which is subjected to pressure oil from the lubricating-oil pump tending to open the fuel pump delivery against the control of a powerful spring in the governor head. This arrangement offers the advantage that each diesel motor stops automatically should the pressure of the lubricating oil fall below a predetermined minimum. The engine speed can be adjusted within wide limits by means of a chain wheel, which regulates the governor spring and is actuated by an electro-magnetic speed governor controlled from either of the drivers' cabs.

The Stork–Ganz four-stroke engine has eight cylinders in line, having a bore of 6·71 in. and a stroke of 8·7 in., is of the precombustion chamber type and has a continuous output of 360 metric h.p. at 1450 r.p.m. with an overload capacity of 400 h.p. at 1450 r.p.m.

Cylinders, cylinder-heads (detachable in this case) and the pistons, carrying four pressure- and two scraper-rings, are of cast iron. The cylinder-head contains one inlet and one exhaust valve controlled by push-rods and rockers from a camshaft located in the upper portion of the crankcase; a device is provided, which prevents automatically the play in the valve motion. The eight-throw crankshaft is supported in nine plain bearings; the big-end bearings are also plain bearings. The crankcase is of cast aluminium alloy. Fuel is injected by a Jendrassik pump. A pressure lubrication system is incorporated. For cooling the lubricating oil there is provided a separate oil cooler, placed underneath the floor of the luggage-compartment and through which the air is drawn by an electrically-driven fan.

In this case the engine speed is adjusted by means of a spring-loaded servo-motor piston, which regulates the delivery of the fuel pump and is subjected to pressure oil circulated in a closed system by a pump driven by the engine. The pressure in this system depends on the quantity of oil circulated (consequently on the speed of the engine) and on the resistance in the circuit. In the circuit five openings are provided, each closed by a spring-loaded needle valve, which can be lifted by an electro-magnet controlled from either of the drivers' cabs. By opening one or more apertures referred to, the resistance in the circuit changes, and in consequence the speed of the engine.

A device is incorporated through which the engine is stopped automatically, should the lubricating-oil pressure fall below a predetermined value.

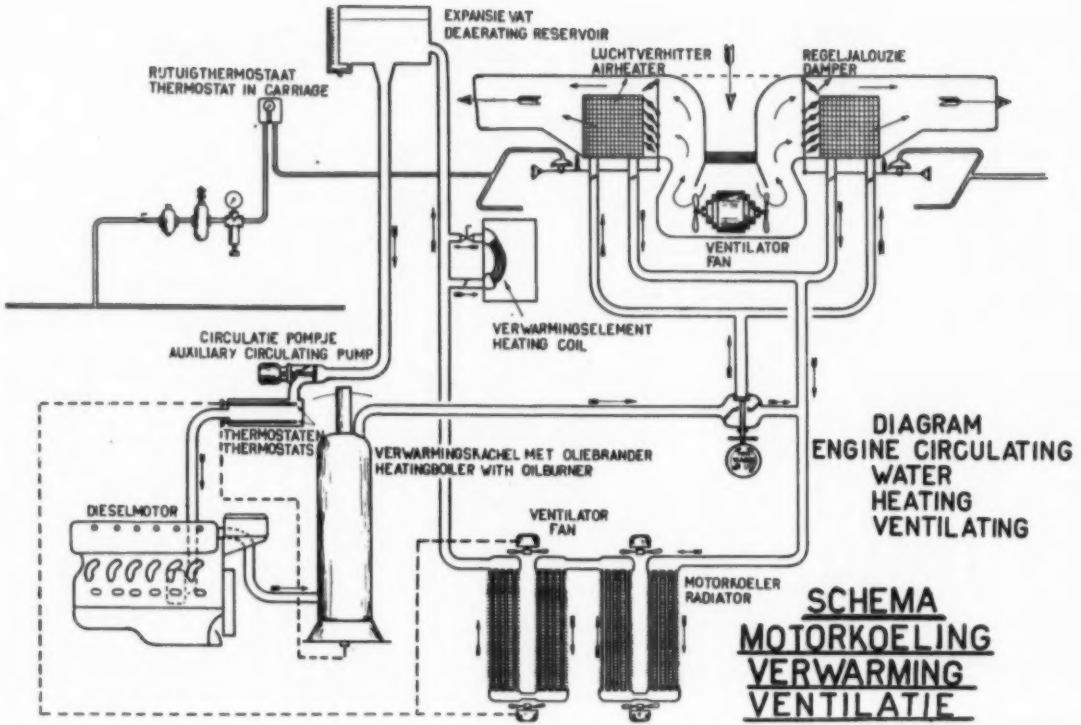

EXPANSIE VAT
DEAERATING RESERVOIR
LUCHTVERHITTER
AIRHEATER
REGELJALOUZIE
DAMPER
RUIMTETHERMOSTAAT
THERMOSTAT IN CARRIAGE
VENTILATOR
FAN
VERWARMINGSELEMENT
HEATING COIL
CIRCULATIE POMPJE
AUXILIARY CIRCULATING PUMP
THERMOSTATEN
THERMOSTATS
VERWARMINGSKACHEL MET OLIEBRANDER
HEATINGBOILER WITH OILBURNER
DIESELMOTOR
VENTILATOR
FAN
MOTORKOELER
RADIATOR
DIAGRAM
ENGINE CIRCULATING
WATER
HEATING
VENTILATING
SCHEMA
MOTORKOELING
VERWARMING
VENTILATIE

Fig. 7.

The weight of the engine is about 3000 kg. (6600 lb.), the fuel consumption at the most economical load about 185 grams per metric h.p./hr.

The cooling-water system, the starting system and the fuel supply from the tanks to the pumps are the same for both Maybach and Stork–Ganz equipments.

The cooling-water system (as referred to above, each motor has its own circuit) is shown in Fig. 7. After leaving the motor the water passes through an oil-fired boiler, then through two air-heaters (in summer-time it is by-passed), next through two radiators placed underneath the floor of the luggage compartment and having electrically-driven fans, through a coil for heating water for the lavatories to a de-aerating reservoir placed under the roof of the engine-room, from which the water returns through a little electrically-driven auxiliary circulating pump to the motor-driven circulating pump. The oil-burner and the fan from one cooler are thermostatically controlled, the fan of the other cooler can be switched on and off by hand.

Before starting the engines, the cooling water is preheated to about 60° C. with the aid of the auxiliary circulating pump and the boiler. There seems to be reason to believe that the absence of troubles with seizure of pistons, encountered elsewhere with the Maybach engines, is due to this preheating of the cooling water before starting.

The exhaust gases pass to silencers mounted in the lower part of the engine-room, from which the gases escape through exhaust pipes terminating above the roof of the coach.

Two fuel tanks, one for each engine, with a capacity of 900 litres (200 gallons), are placed in the lower part of the engine-room. The fuel is delivered to the pumps by air under pressure, supplied to the tanks.

The engines are started electrically, current being supplied for this purpose to the main generator by a 90-cell 200-amp.-hr. Nife battery.

With reference to the choice of 70 Maybach and 10 Ganz engines as motive power, the following is of interest. At the time the order had to be placed (February 1933) a light-weight, high-speed engine was wanted. The Maybach engine was the only one of this type which had been actually in service for some time. Furthermore, the Maybach engine was held to have three distinct advantages, viz. the roller bearings (at that time plain bearings in high-speed engines being not reliable), the cylinder-head being integral with the cylinder, and the absence of a separate oil-cooler.

After three months' service the main roller bearings and also, to a less extent, the big-end bearings began to give way. After a thorough investigation by the firm of Maybach it was proved that the troubles with the main roller bearings were due to overload. The total load of a main bearing has three components: one from the centrifugal forces, one from vibrations and one from the combustion pressure. Regarding the last-mentioned component, it should be remarked that the rate of pressure-rise at the beginning of the combustion and also the maximum pressure were fairly high.

Maybach has now provided the crank axles with counterweights. Taking into account the performances of the motors with counterweights in service, the troubles with the main bearings seem to have been overcome. The first two motors with counterweights put in service have now run nearly 90,000 kilometres without giving any trouble. Improvements made in the

fuel pump and the injection nozzles have diminished considerably the maximum pressure and the rate of pressure-rise of the combustion.

The units are now running daily about 600–700 kilometres (370–435 miles). Light inspections and running repairs are made every seventh day. Inspection of cylinders and pistons with rings takes place after 50,000–60,000 kilometres (31,000–37,200 miles). General overhaul is now expected to be necessary after about 100,000 kilometres (62,000 miles).

DIAGRAM MAIN CHARACTERISTICS POWER TRANSMISSION DUTCH DIESEL-ELECTRIC TRAINS.

PRINCIPE SCHEMA DIESEL-ELECTRISCHE RIJTUIGEN N.S.

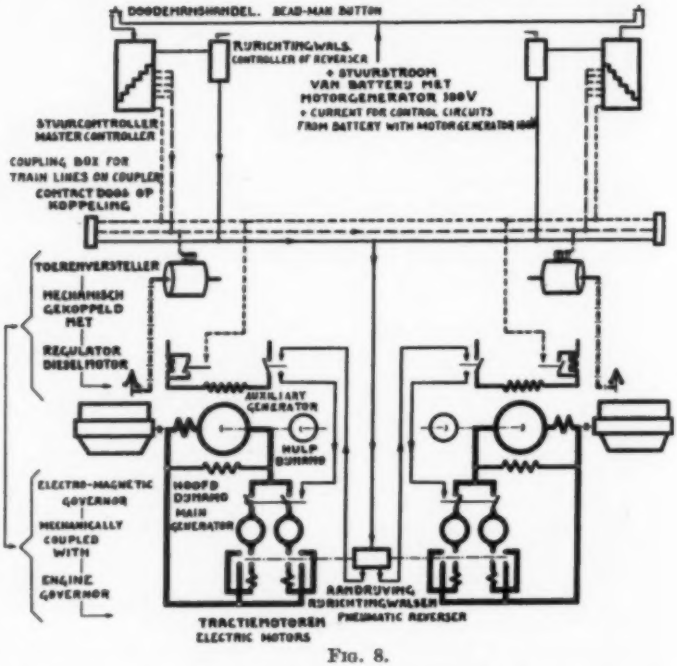


FIG. 8.

Taken over a longer period, the fuel consumption in service per engine is 0·62 litre per kilometre (0·22 gallon per mile), the consumption of the oil-burner included, and the lubricating-oil consumption 1·93 litre per 100 kilometres (0·68 gallon per 100 miles). As regards the last-mentioned figure it is to be taken into account that the oil in the sump is changed every 10,000 km. (6200 miles).

The Ganz engines being an entirely new design in February 1933, it was not thought advisable to fit all the units with these engines.

With the Ganz engines there were some minor troubles. In service it proved difficult to hold tight for long the packing between cylinder and cylinder-head. Also the flexible elements in the pipes leading to and from

the lubricating-oil cooler gave considerable trouble. As to the bearings, no trouble occurred. A short time ago there arose the difficulty of rapid incrustation of the piston rings; a new type of rings is now being tried. On the whole the Ganz motors have worked satisfactorily.

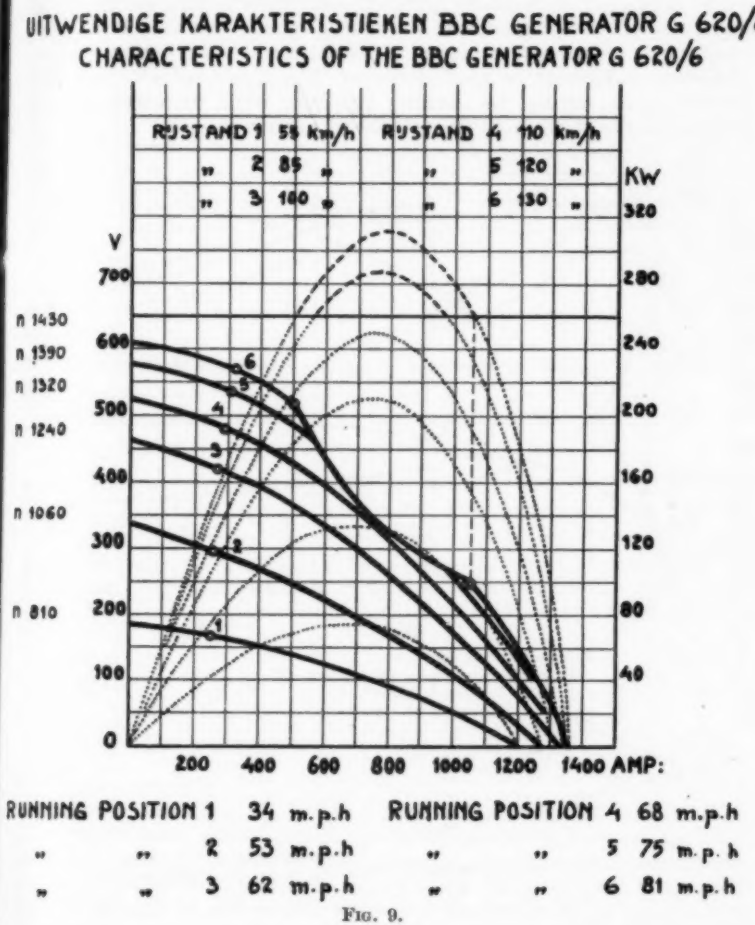


FIG. 9.

Each diesel motor drives an electric generator through a flexible coupling. Current from each generator is led directly to two electric motors, one in each driving bogie.

The lay-out of the B.B.C.–Heemaf equipment is based on Gebus principles, with the slight modification that the generator is not only self-exciting, but also has a constant field of 100 volts (see Fig. 8). The generator has a capacity of 240 kW.; its main characteristics may be taken from Fig. 9.

An auxiliary generator driven directly from the main generator shaft supplies current for lighting, control circuits, cooling and ventilating fans, air-compressors, oil-burners, auxiliary circulating pumps and battery charging.

The voltage of the auxiliary generator and of the battery not being constant, a small motor generator set with a voltage regulator is supplied, which gives a constant voltage of 100 volts for lighting, control current, oil-burners and field of the main generator. The other auxiliaries previously referred to are fed by the auxiliary generator when the diesel motor is running, and by the battery when the diesel motor is stopped.

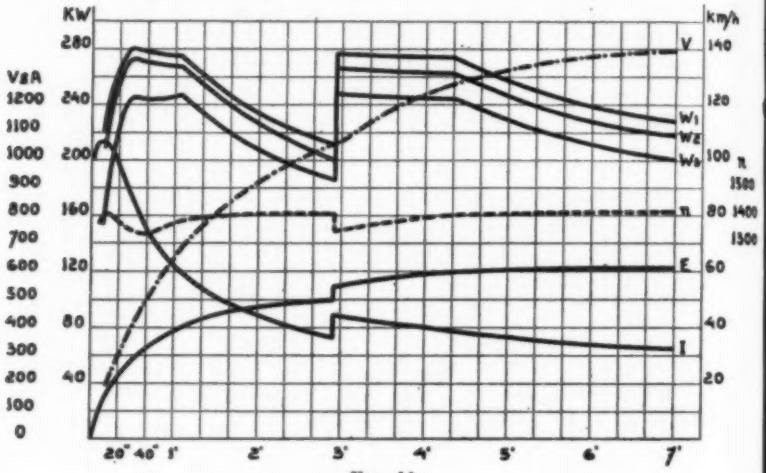


FIG. 10.

V = Speed in km./h.
W_1 = Power Delivered by Diesel Motor
W_2 = Power Consumed by Generator
W_3 = Power Delivered by Generator
n = Number of Revolutions Diesel Motor
E = Voltage Generator
I = Current Generator
} On Time Base.

The power delivered to the electric motors is regulated by raising or lowering the speed of the diesels in accordance with the car-speed required. The range of engine speeds in service is from 1400 r.p.m. down to about 1000 r.p.m.; idling speed is 800 r.p.m. The lay-out is such that in the speed range above-mentioned the motor can be run at five pre-selected speeds, viz. about 970, 1150, 1250, 1330 and 1400, the output being (with the auxiliaries included and the car running at constant speed) respectively about 210 kW., 155 kW., 130 kW., 100 kW. and 70 kW.

In Fig. 10 are shown the changes from car-speed, engine and generator output, engine revolutions, voltage and current of the generator on time base, when starting up the car from standstill to full speed, with both engines running at the highest speed; at this speed strong field is used for the generator from a speed of about 90 km.p.h.

As will be seen from the diagram, the maximum speed obtained is 140 km./h. (87 m.p.h.); under the present schedules the maximum speed is limited to 100 km./h. (62 m.p.h.).

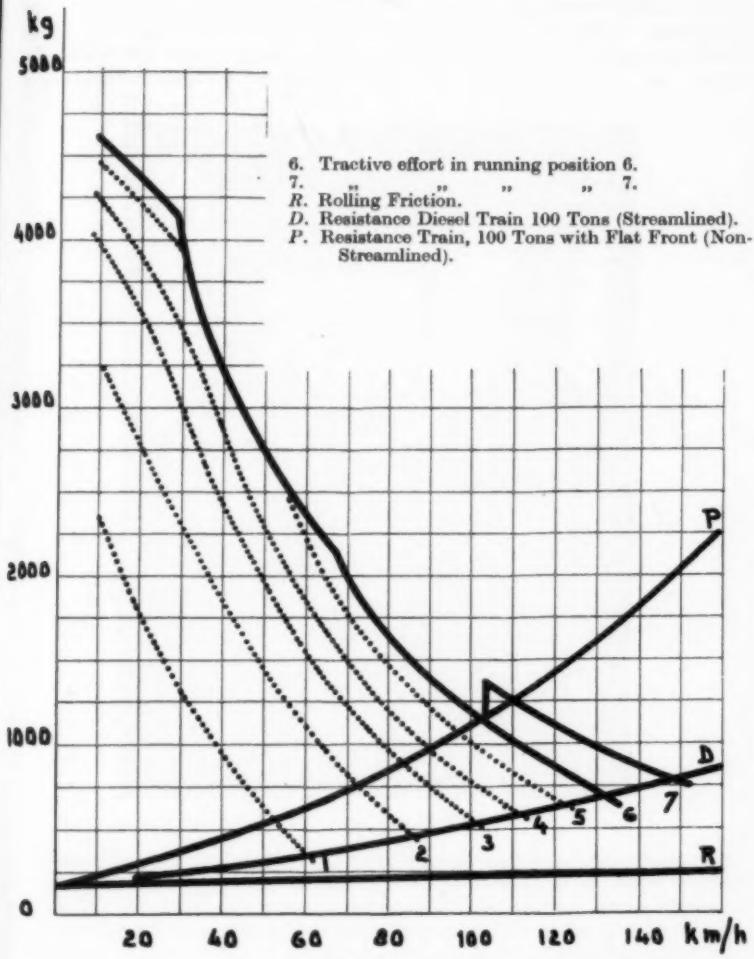


FIG. 11.

Regarding Fig. 11, this is self-explanatory.

A description of the Westinghouse–Smit electrical equipment is thought superfluous, this being not fundamentally different from the B.B.C. equipment.

Cab Equipment.

From the photograph shown in Fig. 12 and the plan view of Fig. 13 the general arrangement of the cab will be clear.

The master controller has two drums: the larger one provides for the variations of the engine revolutions, the operating handle having six running positions, the first five each corresponding with a different speed of the engines, the last one only applying strong field to the generators

Fig. 12.

(whereby the engines maintain the same speed as in the foregoing position), a neutral position and an "off" position. The smaller drum, which can be moved only when the operating handle of the larger drum is in neutral, has five positions: "start engine I," "forward," "neutral," "reverse" and "start engine II."

Multiple-unit train operation is applied, so that two three-car units coupled together, or even more when desired, can be controlled by one man from a single cab. Cooling-water temperatures and engine revolutions of the four engines from two three-car units coupled together are indicated on the measuring instruments in that cab, from which the train is controlled;

the two upper ones of 6 and 7 in Fig. 13 give the indications from the first, the two lower ones from the second unit.

As will be clear from the foregoing, the whole arrangement is such that two three-car sets coupled together can be fully handled and controlled by one man only, this man having before him all the indications he needs for supervising the four engines (revolutions and circulating water temperatures) and capable of starting and stopping each engine from his cab.

An air-operated window-wiper is applied.

A hand-brake control is provided.

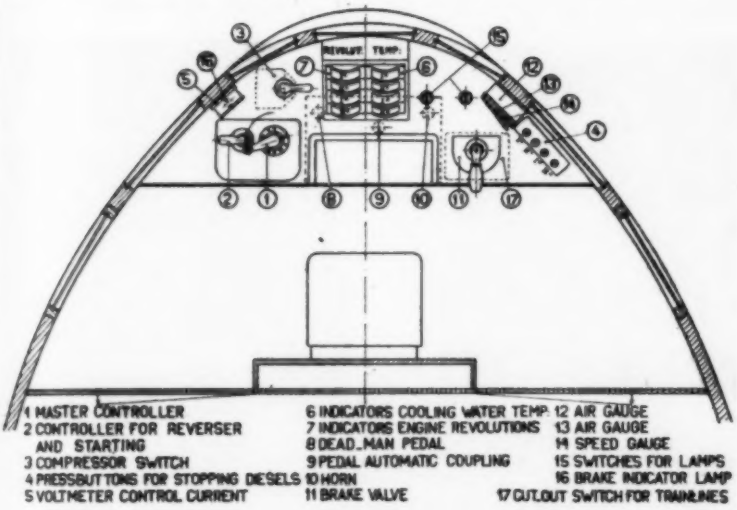


FIG. 13.

If the driver releases the dead-man's handle or the pedal below, the engines, when running in a certain position, are brought back to idling, and rapid braking is applied immediately.

AUTOMATIC COUPLER.

Automatic couplers of the Scharfenberg–Unirop type developed by Scharfenberg in co-operation with the Dutch Railways are applied, which make it possible to couple or uncouple two three-car units in the shortest possible time. The coupling is effected by a simple running together of the vehicles, whereby at the same moment the drawbars, the air-brake conduits and the control train-lines (Fig. 14) are coupled.

For release the driver depresses a foot pedal in the cab, thereby giving access of air under pressure to two cylinders, one putting out the mechanical coupling and closing the air-brake conduits, the other actuating a cut-out switch, which disconnects a certain number of train-lines; after that one or other of the units may move away.

Brakes.

Knorr Lambertsen air-brakes are fitted. This system comprises two train pipes, a brake pipe and a feed pipe. The equipment permits of graduated application and release. Further, the brake is of the drum pattern. Two brake shoes with Ferodo friction linings act on a drum attached to each wheel, each shoe having its own brake cylinder. All the brake cylinders on each bogie are supplied from a common auxiliary air reservoir through a triple valve.

The maximum air pressure in the brake system is 72 lb. per sq. in. (in the main reservoir up to 143 lb. per sq. in.), and the air is supplied by two

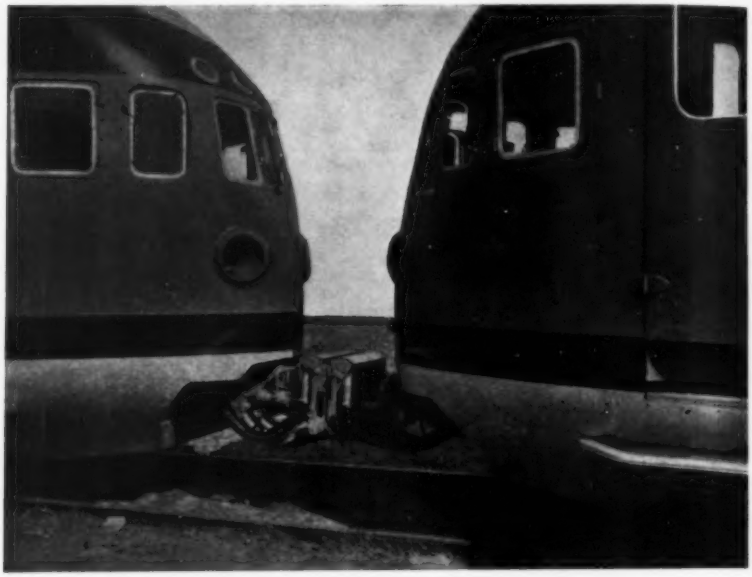


Fig. 14.

electrically-driven compressors which also provide the air for the horns, the pneumatic reverser and for the air pressure in the fuel tanks.

On each bogie is fitted a little switch, actuated by a piston which is subjected to the pressure of air in a pipe connecting two brake cylinders with the triple valve. When one or more of these switches are closed—which happens by applying the brakes—a little lamp lights up in the driver's cab; by releasing the brakes, the switches open and the lamp is extinguished. The drivers are instructed not to start the car so long as the lamp is alight.

Heating and Ventilating.

The heating of the passenger compartments is effected by air, which is raised in temperature by the engine cooling-water in special air-heaters.

The air (Fig. 7) is drawn from the outside through a filter by a fan, is blown through the air-heater and then conveyed through ducts to the various compartments, where it is discharged by openings located under the seats near the sides. The temperature in the carriage is regulated by a thermostat, acting on a damper, which is placed before the air-heater, and regulates the flow of air through the air-heater and a by-pass.

In summer-time fresh air from the outside is blown through by fans fitted under each of the end-coaches.

THE DESIGN OF FUEL INJECTORS FOR DIESEL ENGINES.

By Ir. G. J. Lugt.*

The function of the fuel injector in a diesel engine is to introduce the fuel into the cylinder under the conditions most suitable to give the best combustion and the most economical results. For this purpose the fuel must be given a certain speed and direction, causing an appropriate distribution of the fuel over the available air in the compression space of the cylinder.

The fuel can be injected either pneumatically or mechanically. Mechanical injectors can be classified in two kinds, open and closed injectors.

The closed injector is an apparatus generally consisting of a needle valve, moving with very little clearance and without packing in its guide, a valve seat and a nozzle. The diameter of the spindle of the valve is larger than the diameter of the valve seat, and the fuel which enters the injector between the guide and the seat opens the valve, when the pressure on the differential surface is more than the load of the spring, pressing on top of the valve spindle. Underneath the valve seat is a central hole ending in one or more small holes forming the injecting nozzle. Typical closed injectors are illustrated in Figs. 1 and 2, and represent types of injectors manufactured by Messrs. Robert Bosch of Stuttgart, Germany.

The open injector, by negative definition: a closed injector without spring-loaded valve. This, of course, is simpler in construction and cheaper to make, but the difference in cost is only small, and the functional drawbacks are such that this economy is not justified.

The design of pneumatic injectors will not be dealt with in this paper, as the air-injection diesel engine has practically disappeared from the building programmes of diesel engine manufacturers, and the injectors for this type of engine have only an historical interest. For similar reasons, closed injectors being now almost exclusively used, the open injector will not receive any further attention in this paper.

The function of the fuel injector in a diesel engine is, as above defined, the distribution of the fuel over the air in the compression space of the cylinder. There is no doubt that the pneumatic injection fulfilled this purpose admirably well, and this method therefore held the field for a considerable time. However, it is worth while noting that of the two types of fuel injection, pneumatic and mechanical, the latter has historically the first rights as it was known well before Diesel gave the watchword: air injection.

The precursors of Diesel: Ackroyd-Stuart, Capitaine and others used it, and it can even be upheld that Diesel kept progress back by impressing on the technical world the axiomatic principle that no satisfactory fuel

* Paper presented for discussion at a meeting of The Institution of Petroleum Technologists and The Koninklijk Instituut van Ingenieurs at The Hague, 9th May, 1936.

injection was possible without the use of compressed air. It seems that Diesel's dictum so overawed the designers and experimenters of his time that scarcely any attempts to prove its fallacy have been made during Diesel's lifetime. It was a British firm, Messrs. Vickers, which first disengaged itself from the grip of Diesel's authoritative word. Mr. MacKechney, director of Vickers, made the first attempts of commercial value at mechanical injection in diesel engines, and was, we believe, the coiner of the word "solid" injection. These attempts were crowned with a

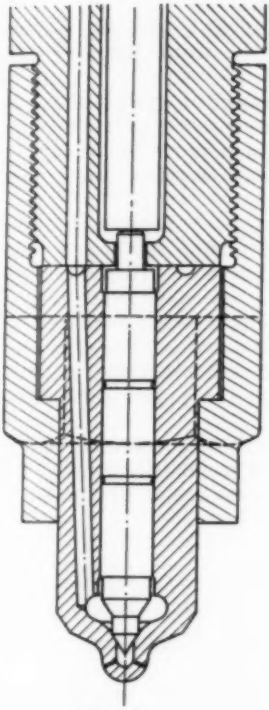


FIG. 1.

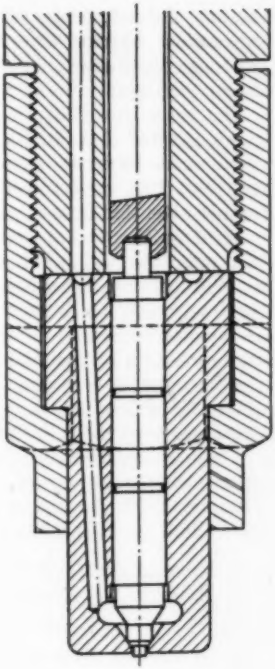


FIG. 2.

measure of success, not sufficient, however, to induce other designers to follow suit immediately. It took ten years, including, it is true, five years of world war, before the solid injection was taken up seriously by the foremost diesel engine builders, and almost twenty years before some of the best-known makers of large marine engines adopted it. An important exception must be made for another British firm—namely, Messrs. Doxford—who may be proud of the fact that they used mechanical injection from the very first and with the most marked success.

There is, of course, a big difference in principle between the pneumatic and the mechanical injection, the former being characterized, as its name

implies, by the use of compressed air for introducing the fuel into the cylinder and for its atomization. But it is worth while to establish the fact that also in the case of mechanical injection it is, after all, compressed air which causes the atomization: the air in the compression chamber of the engine. The real and essential difference between the two injectors is therefore that, in case of the pneumatic injector, the fuel is atomized by the air mixed with it *before* entering the cylinder, whereas in the case of the mechanical injection the atomization takes place by the air *in* the cylinder. To call a mechanical injector an atomizer is therefore a misnomer. Indeed, there is no atomization when there is no air, and a mechanical injector, injecting into a vacuum, gives a solid jet, without any dispersion over a long distance. This will be discussed further in a later paragraph.

The valve in a closed injector is sometimes operated mechanically, but it is suggested that this type of valve will ultimately disappear, the automatic valve being so much simpler and having now proved to be entirely reliable. The mechanically operated valve will therefore not receive further attention in this paper.

By definition the main task of the fuel injector is: distribution of the fuel over the induction air. Now, the process of distribution can be divided into two functions: penetration and dispersion. The latter function can again be divided into atomization and spreading. The task of an injector is therefore more explicitly to give the penetration, atomization and spreading of the fuel most appropriate for a certain type of engine. Furthermore, it is required from the injector that the beginning and end of the injection be sharply defined and that the proper distribution continues over the full period of the injection.

These characteristic functions will now be dealt with separately and in their mutual relationship. Under penetration is generally understood the distance which the end of the fuel jet travels in the compressed air inside the cylinder. It is determined by:

a. Pressure on the fuel,
b. Pressure and temperature of the compressed air in the cylinder,
c. Nature of the hole through which the injection takes place.

It is natural, though erroneous, to think that increased fuel pressure materially enhances the penetration as above defined.

The velocity of the fuel at the orifice increases with the square root of the fuel pressure, but at the same time the resistance in the air increases with the nth power of the velocity, n being a figure between 1 and 2. The influence of the higher pressure is therefore almost counterbalanced by the greater resistance, and increasing the pressure proves an inefficient means of getting better penetration, although it incidentally helps atomization. Experiments on penetration have shown that doubling the injection pressure only gave an increase of penetration of about 17 per cent. The penetration changes with the air density, but by no means proportionally. As the compression pressure is generally determined by other desiderata—self-ignition of the fuel, in the first place—varying this pressure cannot be used as an effective means to influence the penetration.

As *a* and *b* have proved ineffectual, the case for penetration would be

hopeless if *c*, the nature of the hole, did not have considerable influence on the penetration and on the character of the injection, *i.e.* the distribution generally. It is primarily the diameter of the hole which matters. The length of the hole is of less influence. Up to a certain ratio between diameter and length of the hole—say about 1 in 4—penetration increases, but proportionally longer holes do not give any better penetration. A jet ejected from a hole of larger bore, however, will travel farther. The fuel particles in the centre of the jet meet with less resistance; they are of larger size, and consequently have more momentum and less specific resistance. This implies that the atomization is impeded; but this is generally of minor consequence, as the highly penetrating jet is usually required on large size engines, where, on account of the slower speed and the ampleness of the time available for the combustion, a very fine atomization is not so essential.

In connection herewith it may be pointed out that it is erroneous to liken the jet of fuel—as is often done—to shot of very small calibre leaving the muzzle of a shot-gun. It has been previously remarked that the fuel leaves the orifice of the hole in solid formation, as can be proved by injecting into vacuum. As soon, however, as the jet meets air in its course, it is broken up into small particles, which will be smaller the higher is the muzzle velocity and the greater the spreading. Theories about penetration and atomization have been built up on the assumption that the first particles leaving the orifice go farthest. These have been proved to be fallacious: in fact, the first particles emerging are immediately swept off their course by the surrounding air of comparatively high density. But, while pushing the air aside, they give the followers a chance to get a little farther, and so on. As Prof. Schweitzer of the Pennsylvania State College puts it: "the leaders do not remain leaders for any length of time; there is a kaleidoscopic change in leadership." The emerging jet, Prof. Schweitzer says, may be compared to an advancing army, emerging from a fortress. The soldiers in the front line are continually being killed off and their places taken by others pushing up from behind, and from a bird's-eye view we see a wedge of soldiers slowly advancing into the enemy's territory. Prof. Schweitzer gives another elucidating simile to illustrate the nature of the spray: If we substitute rock for compressed air, the jet of fuel will gradually bore a hole into the rock, but the speed at which the depth of the hole increases is by no means equal to the muzzle velocity of the jet! Having ascertained that neither the fuel pressure nor the compression pressure is an important point in obtaining the required penetration, and that the nature of the hole is practically the only determining factor, the influence of the size of the hole on the penetration should be studied.

Some tests made to this end indicate the distance over which the ultimate leader will advance, but it is better to determine the spray velocity at various distances from the orifice for various diameters and at constant fuel pressure and air density. For a hole of 25 thousandth of an inch diameter the spray velocity is about 22 per cent. of the muzzle velocity at 3 inches distance, for a hole of 7 thousandths it is about 7 per cent. In both cases stated the length of the hole was twice the bore.

The tests made by Prof. Schweitzer and those made by other experi-

menters give us a clear insight into what happens when the fuel is injected in air at rest. The whole picture will, of course, be quite different when the air is in motion and when the fuel is ignited after entering the cylinder. To study the behaviour of the jet in these circumstances is, it is needless to say, far more difficult, but not impossible.

A recent publication by Dr. Otto Holfelder gives some beautiful photographs of the spray, its ignition and its combustion in various circumstances. These photographs have been taken at a rate of over 400 a second, and show the shape and development of the jet, the time at which the spray is ignited and how the combustion proceeds while the fuel is being injected.

It is, of course, most interesting to study what happens in the fuel injector and how the fuel behaves after having left the nozzle. However, it is a curious fact that, although tremendous changes in the views regarding these points have taken place, there has scarcely been any change in the design of the injectors. Probably because the theory has lagged behind practice and the best design had already been determined experimentally, by trial and error.

The best size and shape of the holes in the nozzle have been found on the engine by results, as judged from fuel economy, visibility of the exhaust gases and torque.

A designer, considering a certain type of engine with a stroke volume V_s, able to develop the power N_e effective horse-power at n revolutions per minute with a fuel consumption q per working stroke, should determine in the first instance the total area a of the holes in the nozzle. If t be the time taken for the injection of the fuel, v the velocity of the fuel as caused by the initial injection pressure and c the coefficient of discharge

$$a = \frac{q}{cvt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The product of the velocity v and the discharge coefficient c is the apparent muzzle velocity v_a, and if the initial pressure be assumed constant for this particular class of engines, v_a will also have a constant value. If, for instance, the initial injection pressure is 300 atmospheres, and the coefficient of discharge 75, the velocity v_a will be about 190 metres per second. The equation (1) can be written

$$a = \text{const.} \frac{q}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The fuel is being injected over a certain crank angle of x degrees, and the time taken by the injection is

$$t = \frac{x}{360} \cdot \frac{60}{n}$$

This angle x has approximately constant value for engines of one class, so

$$t = \text{const.} \frac{1}{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the fuel consumption per effective H.P. for engines of this class at full

torque is constant, the quantity of fuel q injected per working stroke is proportional to the stroke volume V_s

$$q = \text{const. } V_s,$$

and as under these same conditions

$$N_e = \text{const. } V_s n,$$

it follows that

$$N_e = \text{const. } q \,.\, n$$

or

$$q = \text{const.} \frac{N_e}{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the values for q and t from equations (3) and (4) are introduced in equation (2), it is found that the speed n disappears and that

$$a = \text{const. } N_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This very simple formula says that for a certain class of engines the total area of the holes in the nozzle is directly proportional to the power developed, independent of the speed.

How this total area should be divided over the holes and how these should be arranged is a matter of experiment and experience. Here the volume and shape of the combustion chamber are the principal factors to be considered. In the first place, the designer must have definite knowledge of the shape of the fuel jet when it has fully developed in the combustion chamber or differently expressed: of the shape of the hole which is bored into the compressed air by the jet. This shape is, for the ordinary round hole, of sufficient bore-length ratio; a cone with a top-angle of about 20 degrees ending in a hemisphere, as shown in Fig. 3. The several cones should so fill the combustion chamber that they do not reach the walls of cylinder or piston, and that there is sufficient room around each of them to give the air and fuel ample opportunity to come into contact. The number and the required length of the cones can be determined, and as this length is primarily dependent on the size and length of the hole, these dimensions can be fixed.

As a rule, a certain amount of compromise is necessary in order to get the required total area, and the final adjustments must be made on the testbed. Also as regards the angle at which the holes are drilled in the nozzle, considering that the combustion chamber has not a constant shape and volume, but changes both during the injection.

Fig. 3 gives an example of a combustion chamber of a large marine diesel engine of the Werkspoor four-cycle supercharged type of 500-s.h p. per cylinder. When the first engine of this type was tested in the works several nozzles were tried out, and it was definitely found that an 8-hole nozzle was the only suitable one giving smokeless exhaust even at mean indicated pressures of over 140 lb./sq. inch. With a 12-hole nozzle of equal total area the engine could not in any circumstances be made smokeless, this proving that the cones were too close together and too short. The diameter of the holes is 0·85 mm. and the constant in the formula (5) if a be expressed in square millimetres, is 0·0091.

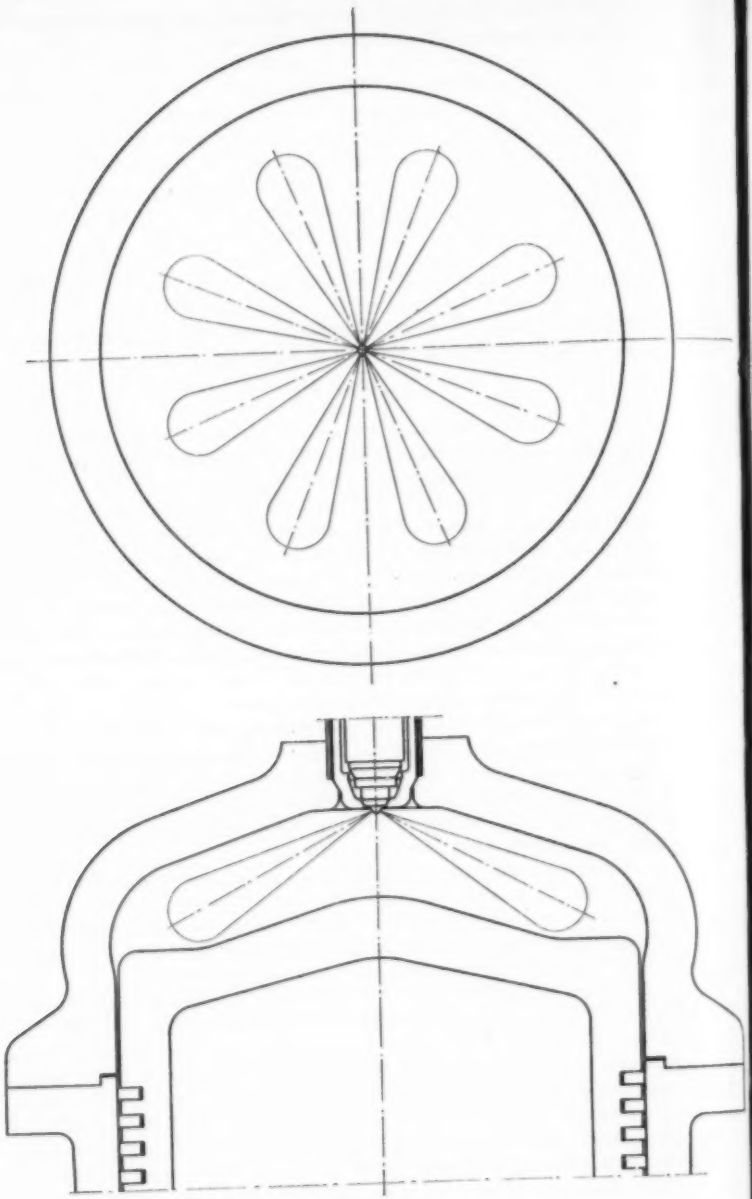


FIG. 3.

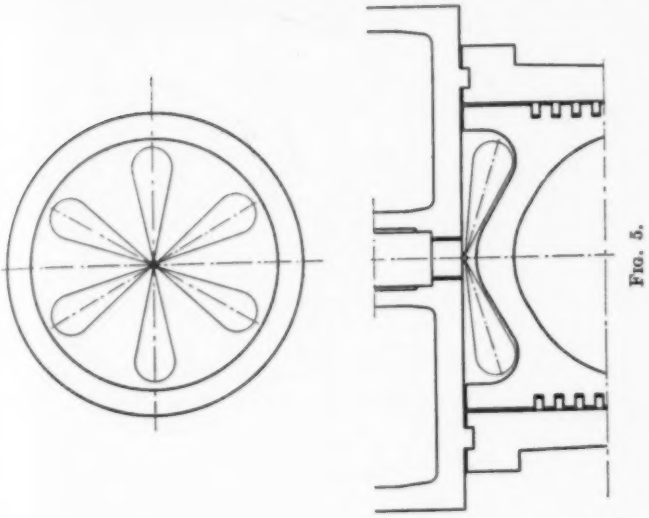


FIG. 5.

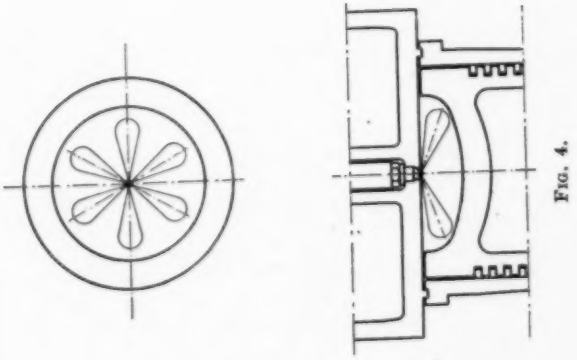


FIG. 4.

Fig. 4 gives another example of the combustion chamber of a Werkspoor cylinder in which 50 b.h.p. is developed at 500 revs. In this case the best nozzle had six holes of 0·30 mm. diameter and the constant is 0·0085, showing that the formula holds good over a very wide range of cases. As the number and the size of the holes can be varied only by steps, it is evident that the constant must show slight variations. The combustion chamber of a Stork–Hesselman–A.E.G. engine is shown in Fig. 5. The form of this combustion chamber is very closely adapted to the shape of the jets, and has been patented by Mr. Hesselman.

It was found that on high-speed engines it is much easier to achieve a good combustion if the air in the combustion chamber is in motion during the injection, if the air is given a certain amount of swirl. The distribution of the fuel must take place in an exceedingly short time, of the order of one-thousandth of a second, and this is made considerably easier if the air is being swept past the fuel orifice. The proper distribution is now obtained by bringing the air to the fuel instead of bringing the fuel to the air. The latter method necessitated injectors with small holes, the size, number and direction of which had to be adapted to a certain most advantageous shape of the combustion chamber. In the former case, given a combustion chamber which causes an air swirl to be developed, the adaptation of the nozzle to the circumstances is much easier. The type of nozzle used is the "pintle" nozzle, which gives a tubular jet, straight or conical as is best suited to the case. These pintle nozzles have the advantage of allowing to work at different speeds with constant pressure, as the needle valve carrying the pintle will lift higher and the area of injection will be increased at higher speeds and vice versa. To describe the means which have been used to produce the air-swirl would lead too far from the subject of this paper; but it may be remarked that among the best solutions found are Mr. Ricardo's "Comet" and "Whirlpool" heads.

Turning now to the design and construction of the injector some cardinal points should be considered.

It is important that the quantity of fuel in the apparatus is as small as possible, and this is essential for that part of the fuel which is entrapped below the valve seat. This fuel can eventually drip out, may carbonize or cause after-burning. The valve should be small and have a low lift, and yet the resistance of the fuel in the valve should be kept at a reasonable figure. There should be no air-pockets in the injector. The entire apparatus should be sufficiently stiff and of symmetrical shape, so that there can be no distortion by heat—or other stresses which can cause an out-of-line of seat and valve guide. These should therefore be either very close together, or the end of the needle valve should be so elastic that it will adapt itself to the conical valve seat. Sometimes the valve seat is made flat instead of conical, in order to cope with the danger of out-of-line of seat and guide. These precautions are the more necessary if the guide, the seat and the nozzle are not made in one body.

The cooling of the injector is an extremely important point, and the injector should be so designed that the cooling is efficient up to the parts which protrude into the cylinder and are subjected to the heat of the combustion. If the nozzle is insufficiently cooled the drops of fuel which

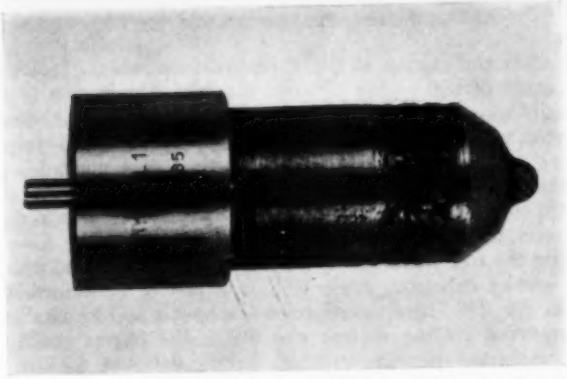


FIG. 7.

FIG. 6.

are formed after the closing of the valve will carbonize. This will spoil the development of the proper jet, will mar the distribution of the fuel and eventually clog up the holes. Some, otherwise excellent, diesel fuels have properties which make a very careful cooling of the nozzle imperative. If kept below a certain temperature—say about 150° centigrade—the fuel will not carbonize, but form a soft deposit which is easily blown off by the spray; but if the nozzle is too hot, carbon deposits will form in the shape of hollow cones, which, hindering atomization and spreading, keep the air from reaching the fuel particles at the proper place and time, which leads in time to smoky exhaust. Some fine examples of cone formation are illustrated in Fig. 6. These were formed in about 8 to 10 hours' running; after an improved cooling system was fitted, the engine could run for practically unlimited periods without carbon deposits forming. It is interesting to note that in this particular case the trouble was at first attributed to distortion of the injectors and to leaking valves. None of the measures taken was capable of overcoming the difficulty, until the cooling was carried so low down as to surround the very tip of the nozzle.

On the subject of cooling it may be incidentally mentioned that three cooling media can come into consideration, viz.: water, lubricating oil and fuel. All three have their advantages and their drawbacks, and it is difficult to give a general rule for the use of any of them. Cooling with water has frequently a curious effect on the material of the injector, the cause of which is hard to detect. The surface is eaten away in a manner which strongly reminds one of the effect caused by cavitation, although it is difficult to conceive how cavitation can occur in this particular place. An injector which is thus affected is shown in the photograph Fig. 7.

When oil or fuel is used, no corroding or eroding action need be feared, but both have other disadvantages. With oil, a leaky injector may cause contamination of the lubricating oil with fuel, which may become dangerous if not rapidly detected. With fuel, a leak in the cooling mantle or in the seating of the injector may allow fuel to enter into the cylinder during the suction or scavenging stroke, and this may eventually cause back-firing.

A well-designed injector which embodies the various requirements enumerated is, after all, a very simple apparatus. But in order to work well it should be made with the utmost care and of the best and most suitable materials. It lends itself well to normalization, and it is therefore quite natural that the manufacture of injectors has been taken up by specialists, who can turn them out in large numbers and at comparatively low prices. A vast majority of diesel-engine builders are now using these normal types of injectors. One of the foremost makers of injectors is the firm of Robert Bosch. Their standard designs are reproduced in Figs. 1 and 2, which represent a pintle-nozzle and a multiple-hole-nozzle.

Messrs. Bosch make a large variety of injectors suitable for various sizes of cylinders, the largest having about a thousand times the stroke volume of the smallest. This means that a suitable injector of normal type can be supplied by Messrs. Bosch for every conceivable size of cylinder. Nevertheless, some of the most renowned diesel-engine builders prefer to produce their own type of injector.

The construction of a Werkspoor fuel valve fitted with a normal Bosch

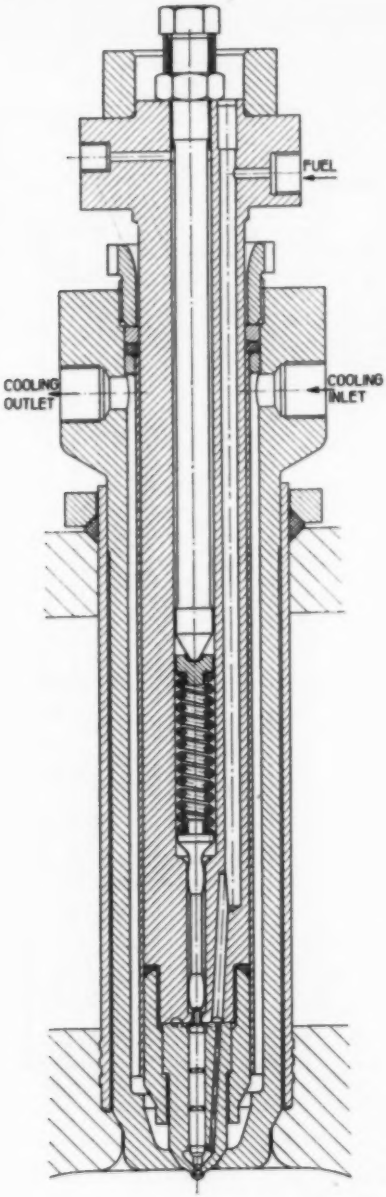


FIG. 8.

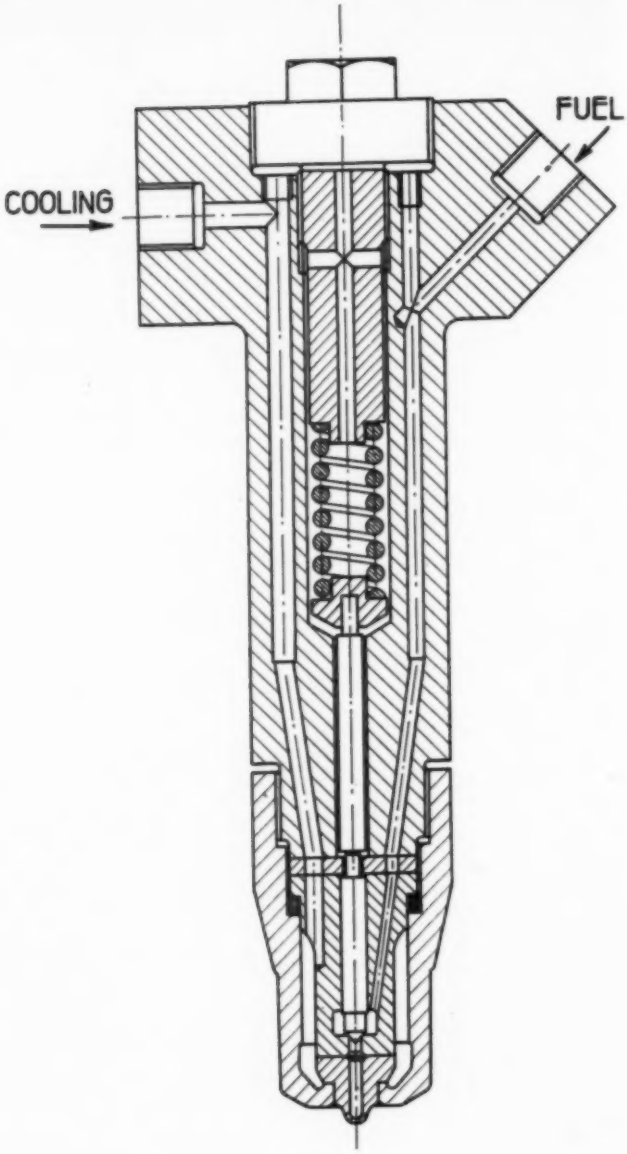


FIG. 9.

STORK NEEDLE VALVE

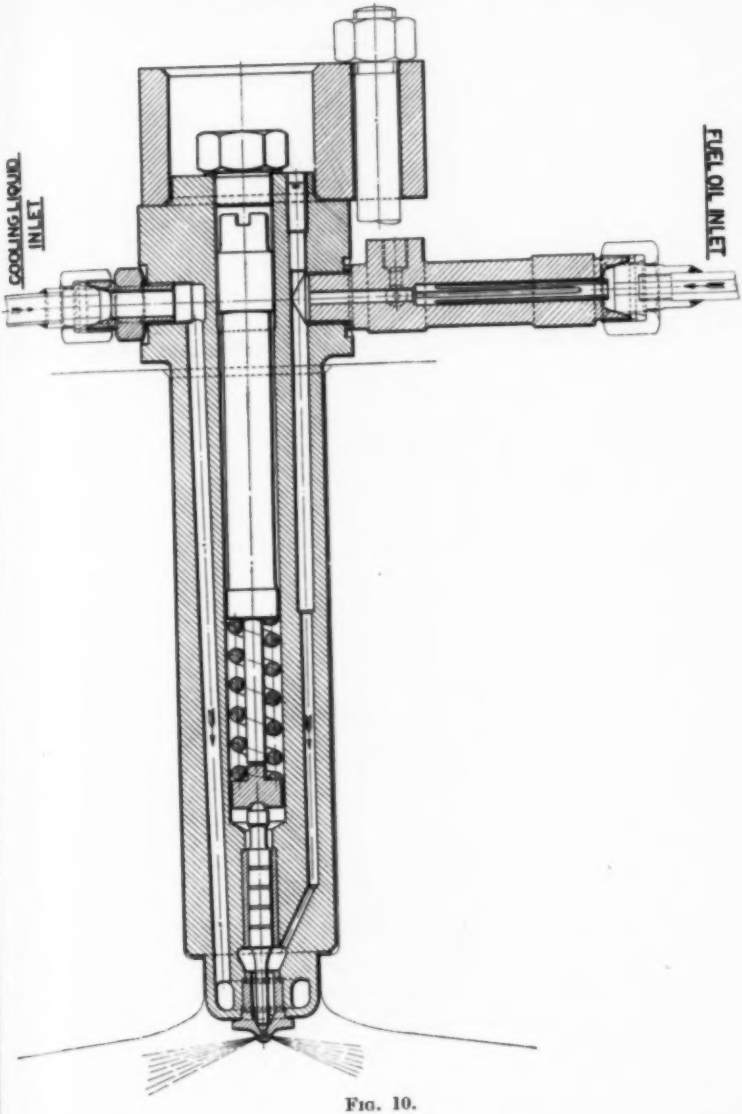


FIG. 10.

STORK–HESSELMAN MEMBRANE NEEDLE VALVE

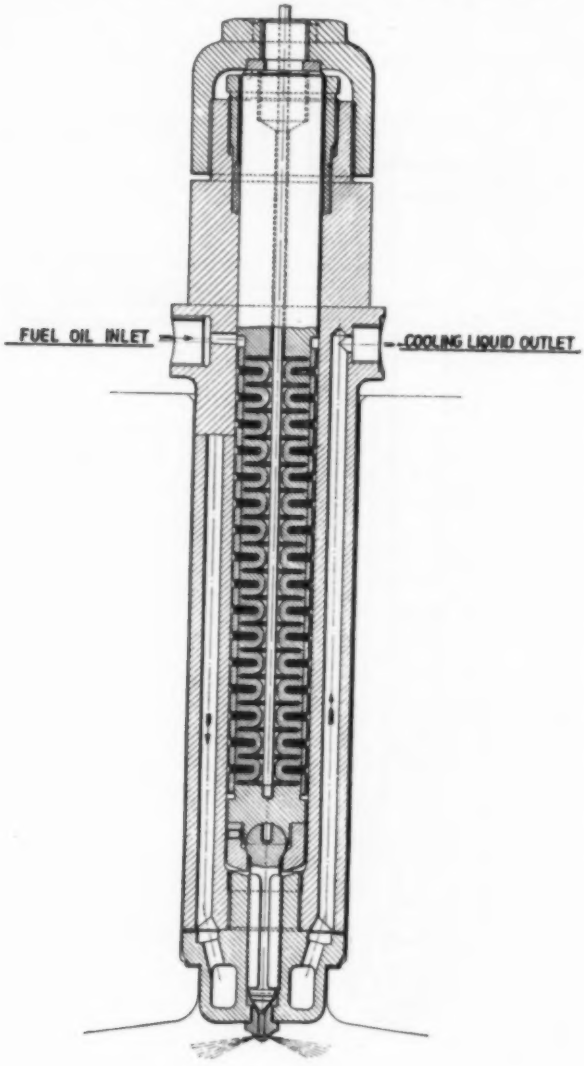


FIG. 11.

injector is shown in Fig. 8. Messrs. Sulzer's design of fuel valve resembles the Werkspoor design very closely, and the injector itself is almost identical with the Bosch injector, but usually of Sulzer's own manufacture.

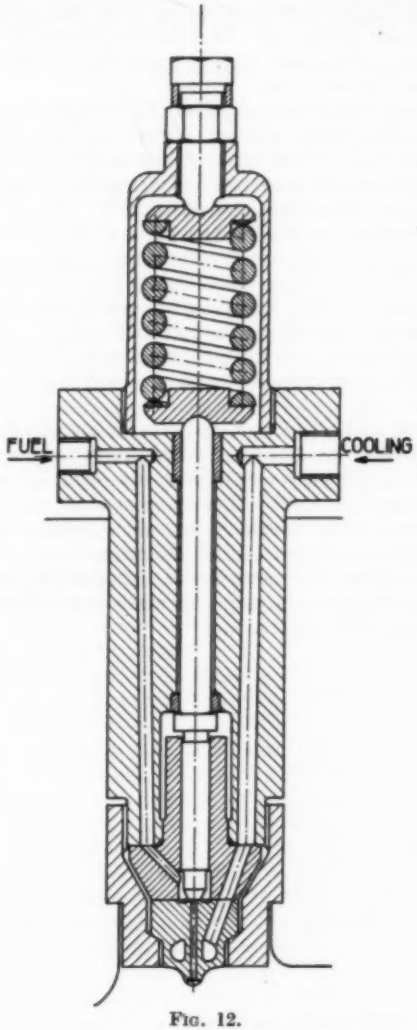


FIG. 12.

Some injectors, the construction of which differs somewhat from the normal Bosch design, are shown in Fig. 9, M.A.N. type, Figs. 10 and 11, Stork–Hesselman type, and Fig. 12, Burmeister & Wain type. In these

designs the nozzle is separate from the valve and its guide. In some the nozzle piece forms the seat of the valve. This construction has the advantage that the nozzles can be replaced without touching the valve, but it means that the seat must be reground when a new nozzle is fitted. This drawback does not make itself felt if the valve has a flat instead of a conical seat as shown in Fig. 12. The Bosch injector has the advantage that there is only one lapped high-pressure joint, whereas the special designs shown have two or three.

An injector which differs radically from the normal in design is the one invented by Mr. Hesselman which is shown in Fig. 11. The valve is fitted to a peculiar type of stiff spring which is built up of steel U-shaped rings. The fuel pressure on the outside of the spring causes it to be slightly compressed, thereby lifting the valve off its seat. The lift of the valve is very small, only a fraction of a millimetre, and the time for opening and closing is therefore extremely short. The great opening force permits the valve-seat to be made of large diameter, so that sufficient passage area for the fuel is obtained. The difference of opening and closing pressure is comparatively small. The design is certainly ingenious, and its advantages may be appreciated, but the construction is rather complicated and costly. The advantages scarcely seem to justify this extra cost and complication.

To conclude, the author wishes to express his opinion that there is little reason nowadays for a diesel-engine manufacturer to design and make his own injectors, unless for very special purposes—as little reason as there is for him to manufacture himself ball bearings or other standardized fittings. Even if he follows the easier course of choosing an injector from a catalogue, he will be left with the difficult task of determining the correct size, shape, and number of the holes in the nozzle for a proper distribution of the fuel in the cylinder, ultimately giving the clean and efficient combustion, which is his one and only object.

DIFFERENT METHODS OF ASSESSING THE IGNITION QUALITY OF DIESEL FUELS.

By F. H. Garner, M.Sc., Ph.D., F.I.C.

The purpose of this paper is to give a summary of the more recent work on the rating of diesel fuels from the point of view of ignition quality.

At the World Petroleum Congress held in London in 1933 [1] a series of papers was presented summarizing the work carried out by workers in various countries on the method of rating fuels for high-speed compression-ignition engines from the point of view of ignition qualities. Papers were presented by Stansfield, Becker and Stacey, Pope, Boerlage and Broeze, giving a general summary of the situation in 1933.

The earliest form of test for ignitability of diesel fuels was the apparatus for the measurement of spontaneous ignition temperature, of which the form devised by Moore is perhaps the best known. Partly owing to difficulties in obtaining concordant results and partly owing to the lack of correlation with actual engine performance, this method has fallen into disfavour in place of simpler tests, such as aniline point or diesel index, or of actual engine test. In some of the later forms of apparatus for the measurement of spontaneous ignition temperature, particularly those in which pressure is taken into account, the apparatus and methods are almost as complicated as the engines and test methods used for the measurement of ignition delay angle. In connection with spontaneous ignition temperature measurements, it has recently been shown that as the average boiling point of petroleum fractions rises, the spontaneous ignition temperature falls to a minimum for the kerosine–fuel oil range, and that after this point a rapid rise takes place in the lubricating oil fractions.[2]

Of the simpler tests for the determination of ignition quality, the Sub-Committee on Diesel Fuels of the Institution of Petroleum Technologists reached the conclusion that aniline point was of value as a method of classification, and this method is now being adopted temporarily in the revised specifications for Diesel Fuels of the British Standards Institution, where a minimum of 60° C. aniline point is specified for high-speed diesel fuels. It is felt that aniline point is quite a useful guide in so far as diesel oils of petroleum origin are concerned, but that aniline point is of no value for oils of other origin, such as shale or coal oil. (The aniline point is related, to some extent, to the paraffinicity, that is, the carbon–hydrogen ratio, of fuels, but is not reliable, inasmuch as with differences in the structure of hydrocarbons the aniline point may not be related to the behaviour in diesel engines.)

Becker and Fischer [4] suggested the use of diesel index as a measure of the ignition quality of diesel fuels, which is expressed as follows :—

$$\frac{\text{Aniline Point in } ^\circ\text{F.} \times \text{A.P.I. Gravity}}{100}$$

and this was shown to correlate with critical compression ratios for a series

of fuels which included both cracked and straight-run products from asphaltic, paraffin and mixed base crude. This method has been used for the last three years, and serves as a simple guide for the rating of ignition quality of diesel fuels, which is adequate for ordinary purposes.

Other tests have been proposed, notably the viscosity–gravity number, which depends on specific gravity and kinematic viscosity, and the formula proposed is the modification by Moore and Kay [5] of that originally proposed in connection with lubricating oils by Hill and Coats [6] in 1928. The number is determined by the following equation

$$G = 1{\cdot}082\,A - 0{\cdot}0887 + (0{\cdot}776 - 0{\cdot}72A) \times \log\log(KV - 4)$$

where G = specific gravity at 60° F.

A = viscosity–gravity constant,
KV = kinematic viscosity in millistokes at 100° F.

A simpler boiling point–gravity number has been suggested by E. A. Jackson, which is calculated from the A.P.I. gravity and the boiling point on the A.S.T.M. distillation curve in °C.[7] The number is determined by the following equation :—

$$G = A + (68 - 0{\cdot}703A)\log BP,$$

where G = A.P.I. gravity in degrees,

A = boiling point–gravity constant,
BP = 50 per cent. boiling point on A.S.T.M. distillation curve in degrees Centigrade.

Heinze and Marder [8] have proposed the use of parachor, which was first suggested by Sugden [9] as a method of determining molecular constitution; these authors use a simplified formula :—

$$\text{Specific parachor} = \frac{\gamma^{0{\cdot}25}}{\text{specific gravity}}$$

where γ is the surface tension, and claim that specific parachor correlates well with cetene numbers.

Stansfield, in the World Petroleum Congress in 1933, described a method of rating diesel fuels in a single-cylinder Gardner engine, type LW, in which two sets of tests were made, (1) delay angle measurement, and (2) starting tests. It was found that ease of starting was connected with sweetness of running, but both types of tests appeared to be necessary in order to rate fuels properly.[10] Pope, at the same time, described the work carried out by the Waukesha Motor Company, leading to a method of measuring critical compression ratio at which audible combustion at the exhaust port could just be detected when fuel was injected into the combustion chamber of a modified C.F.R. engine motored at 600 r.p.m.[9]

Dumanois about the same time suggested the use of heptane values, which are determined in the C.F.R. engine by the standard procedure used for the determination of knock ratings. The fuels used were blended with gasoline in the ratio of 15 : 85, with cooling liquid temperature of 150° C., the engine being run at a speed of 500 r.p.m.[12]

It is not intended in this brief paper to describe, except in outline, the work that has been carried out on the rating of diesel fuels in engines. The ignition delay angle has probably been more widely used than the other three methods mentioned, and attention has been concentrated on methods of measuring the time of injection and the time when ignition occurred. Recently the cathode-ray tube has been applied in the development of more precise indicators, more particularly the Metrovick–Dodds Indicator [13] and the Sunbury Indicator,[14] and such indicators have a definite field in the testing of diesel fuels.

Boerlage and Broeze, as a result of a very comprehensive investigation, put forward to the World Petroleum Congress in 1933 [15] a method using a Maihak indicator, and described the adaptation of the bouncing pin of a C.F.R. engine for the measurement of ignition delay angle.

In earlier papers and before the Society of Automotive Engineers [16] these authors first suggested mixtures of cetene and mesitylene for the rating of diesel fuels, and these were later changed to cetene and α-methylnaphthalene.[17] Cetene number is defined as the percentage of cetene in the standard fuel blend which matches the sample tested, and it was pointed out that for everyday work cheap sub-standard fuels calibrated in terms of cetene were used.

The Volunteer Group for Compression Ignition Fuel Research,[18] comprising representatives of the leading oil companies in the United States, Bureau of Standards, Yale University, Massachusetts Institute of Technology, reported in 1935 that, as a result of work on critical compression ratio and ignition delay angle, they found that the critical compression ratio gives considerable variation in the results: the delay method was found to be less rapid than the critical compression ratio, but was more accurate, and for this work they used the C.F.R. engine converted for diesel operation and for the measurement of ignition delay angle used the knock meter.

More recently [19] this group has reported that cetane has been adopted in place of cetene as the standard method for reporting the results, and sub-standard secondary reference fuels are used in routine testing. The method of test used is the delay angle method, and involves matching the ignition delay determined on the C.F.R. high-turbulence head diesel engine by a suitable bouncing-pin apparatus against the ignition delay of cetane and α-methylnaphthalene mixtures. The results of co-operative tests between thirteen laboratories for nine samples were surprisingly good, showing a grand average deviation of the order of $\pm 1\frac{1}{2}$ cetane numbers.

Reference should be made to the paper by Schweitzer and Hetzel [19] presented at the same meeting of the S.A.E., in which a special piece of apparatus which is claimed to be superior to the bouncing-pin was described. The moment of ignition is determined by a mechanism consisting of a diaphragm in the cylinder wall, a phonograph "pick-up," a short stiff wire transmitting the motion of the diaphragm to the pick-up, a thyratron relay and a neon lamp protractor. When ignition occurs in the cylinder the diaphragm is flexed, and the velocity of flexing is sufficiently high so that the voltage generated permits a high-tension condenser discharge to be sent through the neon lamp, which thus, by its flashes, indicates the time of ignition.

Recent work has again directed attention to the comparison between the

various physical methods for determining ignition quality, and the ignition quality as determined by cetene or cetane number. The Technical Committee "C" on Fuel Oil of Committee D-2 of the American Society for Testing Materials has put forward [20] a classification for diesel fuels based on certain tests, including ignition quality. For the latter test, cetane number, diesel index number, viscosity–gravity constant and boiling-point constant are suggested. It is stated that more reliable results may be possible when using cetane rather than cetene. The following table is quoted as giving the approximate conversion from cetane number to the other methods quoted for rating ignition quality :—

	Oil Grades.		
	No. 1–D.	No. 3–D.	No. 4–D.
Cetane number (min.)	50	40	30
Diesel index number (min.)	45	30	20
Viscosity–gravity number (max.)	0·86	0·89	0·91
Boiling-point–gravity number (max.)	188	195	200

Hubner and Murphy [21] have recently published a comparison of engine rating and calculated ignition quality factors for a large number of diesel fuels, both straight- and cracked-run, and 50/50 blends of the straight- and cracked-run, together with doped fuels. They state that of the several ignition quality factors listed, blending octane number, diesel index, viscosity–gravity constant, etc., blending octane number appears to give the closest correlation with cetene ratings, not only for petroleum fractions, but also for doped fuels and cetane-α-methylnaphthalene blends. They quote an instance of three straight-run fuels from Pennsylvania, Michigan, and a specially selected oilfield respectively, of which the cetane ratings by the delay method were found to be 62, 68 and 74 respectively, in which the viscosity–gravity number, boiling-point–gravity number and diesel index number failed completely to repeat the results of engine tests.

A more recent paper by Reiter and Avanzini [22] using a modified C.F.R. engine and a Series 30 engine showed that in the case of diesel index the maximum divergency from a straight line was 0·2 critical compression ratio, corresponding to approximately 6 on the cetane scale. In the case of Hubner and Murphy's figures the maximum variation in the case of one sample only appeared to be 10 cetane numbers.

Of the various methods for the rating of fuels, the determination of ignition delay angle, either in the modified C.F.R. diesel engine or in some other engine such as the Gardner, is being more and more used as the testing technique is more fully developed. The use of diesel index or aniline point serves as an approximate method for rating normal diesel fuels derived from petroleum, but experimental work shows that these purely physical methods cannot be relied upon to correlate satisfactorily with engine performance even with diesel fuels of wholly petroleum origin.

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DIESEL FUEL SPECIFICATIONS.

By C. H. Barton, M.A., A.I.C.*

The object of diesel fuel specifications is to classify fuels into grades on the basis of viscosity and to indicate the desirable properties of the various grades. To ensure reasonable cleanliness of fuels it is also usual to include limits for such contaminants as water, ash, etc. It is proposed in this paper to examine the significance of the tests commonly employed in fuel specifications.

Viscosity.

The property of viscosity, on which fuels are primarily graded, calls for the first consideration. It is usual, in specifications, to set limits for the maximum permissible viscosity at some arbitrary temperature, such as 100° F., 20° C. or 50° C., for each grade of fuel. Limits are not usually specified for minimum viscosities, and such limits are not, in general, necessary. If, however, very low viscosity fuels are employed, it is worth bearing in mind that unduly high fluidity may give rise to leakage of fuel from pumps and injectors, and may possibly cause too fine a degree of atomization together with an undesirable reduction in the penetration of the fuel in the combustion chamber. The opinion is sometimes expressed that the rate of wear of fuel pumps increases as the fuel viscosity falls, but there does not appear to be much evidence that this factor is important in the range of fuels normally used.

When dealing with fuels of low viscosity it is important to remember that Redwood and Saybolt viscosities below 40 seconds are of little value, since, in this range, the outflow times observed in these viscometers are not accurately related to true viscosities. It is therefore necessary to determine the viscosities of thin fuels in true or absolute viscometers.

If the viscosity of a fuel is too high it will obviously impede the flow of fuel to the pump, and may interfere with the delivery of fuel in air-injection engines and give rise to poor atomization and excessive penetration in solid injection engines. Since the viscosity of fuels diminishes rapidly with increase of temperature, it is possible, by providing temperature control, to adjust the fuel viscosity to the requirements of a given injection system and so make the engine less dependent on the viscosity-grade of its fuel. This is a subject to which relatively little attention has been devoted by engine designers.

Ignition Quality.

The question of ignition quality has attracted much attention since the small high-speed compression-ignition began its rapid development a few years ago. In the early days of the high-speed engine the opinion was

* Paper presented for discussion at a meeting of The Institution of Petroleum Technologists and The Koninklijk Instituut van Ingenieurs at The Hague, 9th May, 1936.

sometimes expressed that the upper limit to the speed of rotation would be controlled by lack of sufficient time for the combustion of diesel fuels at high engine speeds. In point of fact, no such limit has been reached, although small diesel engines have been run up to speeds of 4000 r.p.m. Curiously enough, a difficulty unconnected with rotational speed has persisted in regard to the combustion of fuels in the high-speed engine—namely, ignition delay. Between the start of injection of the fuel into the combustion chamber and the moment at which the fuel begins to burn there is an interval—the delay period—which for a given engine, fuel and injection timing is approximately constant when measured in degrees of crank angle. Now, a long ignition delay allows a large amount of fuel to be injected before burning starts and, in consequence, the rate of pressure rise is high immediately after combustion. The effect of this is to produce rough running and diesel "knock." On the other hand, if burning starts too soon after the beginning of injection, although combustion is relatively smooth and shockless, another difficulty, which will be referred to later, may arise.

Conditions tending to retard combustion naturally lengthen the delay period and accentuate "knock" in a compression-ignition engine. Thus, reduction in the density of the ingoing air by throttling increases the delay and knock. Conversely, supercharging tends to reduce the delay period and to promote smooth running. Since the method of mixing the air and fuel, and their physical condition during the mixing process, have an important effect on the initiation of combustion, it is evident that engine design must have a great influence on ignition lag.

From the point of view of the fuel it has been established that the ignition delay depends on the chemical nature of the oil. Thus, the more paraffinous types of fuel ignite most readily, whilst the more aromatic fuels give longer ignition lag. The requirements of the compression-ignition engine in regard to the chemical nature of its fuel tend to be the reverse of those of the spark-ignited engine in which a high resistance to self-ignition is desirable on the part of the fuel for the purpose of avoiding "pinking" or "detonation." It is important to keep in mind that the limitations imposed by fuel quality on the working of the two types of engine are quite different. In the case of the spark ignited, homogeneous charge engine the power output is definitely limited by the knock-rating of the gasoline. After the onset of a certain intensity of detonation no further increase in output is possible under the prevailing conditions of working, and attempts to raise the output by increasing compression ratio or degree of supercharge act in the direction of intensifying knocking. In the compression-ignition engine ignition delay is most pronounced at low loads. As the engine output and temperatures are increased the delay period tends to shorten and the diesel knock or roughness of running to decrease. Increase of compression ratio or of intake air pressure also reduces the knock. It may be said, therefore, that the power output of a compression-ignition engine is not limited by the ignition quality of its fuel in the way in which the output of the spark-ignited engine is restricted by the anti-knock value of the gasoline on which it runs.

Some reference has already been made to the undesirability of having too short an ignition delay. The basis for this statement is the experimental observation by Boerlage and Broeze [1] that the maximum power output of a

high-speed engine for a just visible exhaust is sometimes lower on fuels of high than on fuels of medium ignition quality. The explanation offered for this fact is that ignition takes place too rapidly on the high ignition quality fuel to allow of adequate mixing of the fuel and air before combustion. Quite apart from the cause of the phenomenon, however, the observation is an illustration of the general statement that the power output of a high-speed engine is not dependent upon the use of a fuel of high-ignition quality. The majority of engines are, of course, only occasionally required to deliver their full power, and, in consequence, smoothness of running is generally more desirable to the operator than 5 or 10 per cent. extra power at the peak load. In view, however, of the high first cost of oil engines, serious consideration must frequently be given to their power output. For automotive engines especially, roughness of running is objectionable, and for this application the demand for fuels of moderately high or high-ignition quality is likely to continue for some time. Furthermore, engines of this type are frequently required to start readily in cold weather. In the absence of the provision of heater plugs in the combustion chamber, the ease of starting is proportional to the ignition quality of the fuel.

Of the various methods of assessing ignition quality which have been proposed, one involving an actual engine test for ignition delay will probably be generally adopted. In order to eliminate the use of the actual delay angles which inevitably vary with the engine, the results are preferably expressed in terms of the composition of a mixture of two standard fuels, the mixture having the same ignition delay as the unknown fuel. This scale for ignition quality, which is analogous to the octane number scale for knock ratings in spark-ignited engines, was first proposed by the staff of the Delft Laboratory,[2] who suggested cetene as the high-ignition quality standard and alpha-methyl-naphthalene as the low quality standard. These substances were chosen because they are chemical compounds which can not only be used as diesel fuels, but can also be obtained in sufficient quantity at a reasonable cost for engine testing. Owing to the chemical difficulties to be overcome in preparing suitable compounds in sufficient quantity and state of purity, no other standards have been proposed except cetane, which has been put forward in place of cetene, by the Volunteer Group for C.I. Fuel Research under the chairmanship of T. B. Rendel in America. A number of methods have been put forward for estimating the relative ignition qualities of fuels from their physical and chemical properties. These tests include aniline point, Diesel Index, Viscosity–Gravity constant, Boiling-point Gravity constant, Spontaneous Ignition Temperature, etc. The data given by the tests afford a reliable indication of the ignition quality for some fuels, but it is invariably found that for a wide range of oils of different types the results in many cases do not give a safe guide to ignition quality.

Fuel Volatility.

Our knowledge of the effect of fuel volatility on the performance of compression-ignition engines is rather meagre. Too high a volatility may, by causing rapid evaporation of the fuel drops, bring about poor penetration and distribution of fuel. At the same time, the volatile fuel may form a

certain amount of homogeneous air/fuel mixture which is capable of producing the pinking or detonation associated with gasoline engines.[3] Generally speaking, in the case of liquid fuels, increasing viscosity is accompanied by diminishing volatility. Consequently, the effect of high viscosity in reducing the degree of atomization and increasing the penetration may also go hand in hand with reduced evaporation of fuel from the spray. As the fuel becomes "heavier," therefore, its tendency to pass through the combustion space without burning increases. The addition of large proportions of heavy fuel to light diesel fuels is prevented by the maximum viscosity requirements of specifications. A further limitation to the presence of heavy fuel in light diesel oil is sometimes imposed by specifying some limit to the distillation properties of the fuel, such as a minimum percentage distilling to say 325° or 350° C. The present state of knowledge certainly does not warrant the use of such limits except for the very lightest fuels for small engines. The general performance of a fuel is, at present, sufficiently well indicated by other properties. As a matter of fact, there is no method in general use for determining the volatility of fuels which can be considered altogether satisfactory. Distillation tests, such as that of the A.S.T.M., are unreliable when the temperature approaches 350° C., owing to the incidence of cracking. A less objectionable test would be a distillation either with steam or under reduced pressure to minimize the tendency to cracking. A coking test, such as that of Conradson, probably affords a better guide to the effective volatility of a fuel, especially in regard to its tendency to form carbon deposits, than does a distillation at atmospheric pressure, such as the A.S.T.M. method.

Coke Tests.

In spite of its somewhat empirical nature, the Conradson coke test appears to indicate fairly well the tendency of fuels to form carbonaceous deposits owing to their lack of volatility. The coke test is not so satisfactory for predicting carbon formation on the atomizer nozzle, but deposits on this part are mostly due to insufficient cooling of the nozzle. It is, of course, true that clean running without formation of heavy carbon deposits may take place in some engines with fuels of high Conradson values,[4] but general experience shows that, under less favourable working conditions, the formation of combustion chamber deposits increases with the Conradson coke value of the fuel. The coke test of a fuel rises as the proportion of high-boiling material which it contains increases. Hence, the addition of a heavy residual fuel to a distillate produces a progressive increase in the coke number and, at the same time, in the "hard" asphalt content, as determined by precipitation with petroleum ether. The Conradson coke value and asphalt content of a series of fuels thus move in parallel. Broadly speaking, the asphalt content is approximately one-half of the coke value, and is a rough guide to the amount of heavy residual oil in a fuel blend.

The asphalt content of a fuel is often taken as an index of carbonizing tendency, and limits to the permissible asphalt in a fuel are accordingly set in specifications. It is worth pointing out, however, that a suitable "de-asphaltizing" treatment will reduce the asphalt content of a heavy

fuel to a negligibly small figure without effecting more than a partial reduction in the coke value of the oil. In such cases the carbonizing properties are generally found to follow the coke value. This is a particular instance of the general proposition that coke value is a surer guide to carbonization than is hard asphalt content.

Sulphur Content.

Fuel specifications commonly include a limit to the proportion of sulphur, the maximum permitted being less for the lighter than for the heavier grades. The sulphur in a fuel is burnt in the engine to sulphur oxides which are acid-forming in the presence of water. The action of sulphur oxides on the engine is at present only imperfectly understood, and doubtless much more information will become available within the next few years. In certain engine installations, in which it is necessary to employ very long exhaust pipes, corrosion of the exhaust system may be enhanced by a high sulphur content in the fuel. It is also probable that engines running with an abnormally low water-jacket temperature, due to an unnecessarily high rate of supply of cold water, suffer from corrosion wear of the cylinder when fuels of high sulphur content are employed. Le Mesurier and Stansfield,[5] from a study of results with marine engines, have reached the conclusion that liner wear is almost independent of the origin, and hence of the sulphur content of the fuel. It is common practice in specifications to fix a limit of 1 or 2 per cent. for the sulphur content of light diesel fuels. The justification for these limits will tend to disappear with the increasing applications of corrosion-resisting metals.

Pour Point.

With the object of ensuring fluidity of the fuel in the supply system at low atmospheric temperatures, maximum pour points are frequently specified. It should be kept in mind that low viscosity fuels are able to flow under quite small pressures at temperatures as much as 5° or 10° C. below their pour points. High viscosity fuels, on the other hand, may be so viscous at a temperature higher than their pour point as to require very high pressures to produce an appreciable rate of flow. In this connection the desirability of temperature control of the fuel system for the purpose of maintaining the viscosity of the fuel within workable limits has already been mentioned. From its nature the pour point gives rather indefinite information. For example, the actual results obtained vary with the test conditions, and frequently with the previous treatment of the oil. When the fluidity of a fuel at temperatures approaching the pour point is of practical importance, the data should be supplemented by viscosity measurements in suitable capillaries.

Ash and Water Content.

Diesel fuel specifications almost invariably contain limits for the ash or non-combustible content, the maximum varying from 0·01 or 0·02 per cent. for light fuels up to about 0·1 per cent. for the heaviest grades. The

nature of the ash-forming material, which is seldom taken into account, is quite as important as the amount present in the fuel. A small proportion of abrasive sand or silica may cause more wear and sprayer erosion than a larger percentage of less abrasive material, such as alumina. The matter of ash content leads immediately to the important subject of clean handling of fuels. The necessity for preventing the access of dirt to fuel storage tanks and for regular inspection for cleanliness cannot be too strongly emphasized. Whenever possible, drain cocks should be provided at the bottom of storage tanks, particularly any tanks in which the fuel remains for more than a day or two, in order that the accumulation of water and dirt in the oil system may be prevented by regular inspection and, if necessary, removal of the tank bottoms.

Restrictions on the percentages of water which are allowed in diesel fuels are quite legitimately included in specifications. In the heavier grades of fuel as much as 0·5 or 1 per cent. water may be tolerated, but in the lightest grades not more than 0·25 per cent. free water should be present. Since the standard methods for water estimation, such as that of the A.S.T.M., are not accurate to less than 0·2 per cent. water, it is evidently difficult to specify smaller water contents than this figure. The principal objection to the presence of small amounts of water in light fuels probably arises from the blockages caused by the water in the dense fabric filters commonly employed in the fuel supply pipes of small high-speed engines. Fortunately, the low viscosity and specific gravity of the fuels involved favour the ready separation of water by settling. The B.S. & W. test, which is really applicable only to the heavier grades of burner fuel, is sometimes used in diesel fuel specifications. The test, however, does not give any useful data additional to that provided by water and asphalt determinations, and the results are not readily duplicated, especially when different samples of the same fuel are involved.

Calorific Value.

Minimum calorific values, generally expressed on a fuel weight basis, are often included in specifications. The chief effect of these limits is to exclude or restrict the addition of such materials as coal distillates to fuels. The calorific values of petroleum oils of the same grade or viscosity vary within rather narrow limits, according to their chemical type and specific gravity. A point that should be kept in mind is that agreement on calorific value determinations between different routine testing laboratories is generally not much better than 1 per cent.

Fuel Filters.

Reference has already been made to the behaviour of water in fabric oil filters. This is one aspect of an important point in the behaviour of light fuels which cannot at present be adequately covered by specification tests. For the slow-speed diesel engine the cleanliness of the fuel may be satisfactorily maintained by reasonable attention to storage conditions, together with the provision of metal gauze filters in the fuel lines. The development of the small high-speed engine has naturally been dependent on the produc-

tion of pumps capable of accurately metering small quantities of fuel at high speeds. Such pumps, with their fine clearances between the moving parts, obviously require protection against minute abrasive particles in the fuel. To effect the removal of these minute abrasives, filters of the felt and woven fabric type have been introduced. These filters have a considerable resistance to the flow of the fuel and, what is more objectionable, they have a marked tendency to become blocked up with small amounts of otherwise innocuous substances such as water and wax. The latter material is present to some extent in most fuels, especially those of the high-ignition quality type, and its separation in the solid state is promoted by a fall in the temperature, which, at the same time, slows down the filtration rate owing to its effect in raising the viscosity of the oil. The ideal filter for high-speed fuel pumps should have the following characteristics in addition to the capacity for removing deleterious materials from the oil : (*a*) smallest possible resistance to oil flow in order to avoid the necessity for using high filtration pressure which may force dirt particles through the filter; (*b*) easy cleaning; and (*c*) the filter should not be susceptible to the blocking action of small amounts of wax or water in the fuel.

Returning finally to the question of fuel specifications, it may be said that the essential points to be covered for a diesel fuel of petroleum origin are the following :

Viscosity at, say, 100° F., 20° C., or 50° C.
Carbon-forming tendency (*e.g.* Conradson test).
Ignition quality (principally for high-speed engines).
Maximum ash and water contents to ensure general cleanliness.

In special circumstances, limits for the pour point or viscosity at low temperatures may be required.

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MODERN TESTING OF MOTOR FUELS FOR THE HIGH-SPEED TYPE OF AUTOMOTIVE DIESEL ENGINE.

By Dr. Ing. A. Hagemann and Dr. Ing. Th. Hammerich.*

The operation of automotive diesel engines calls for varied properties of the motor fuels. In order to develop suitable testing methods, the required properties must first be ascertained, as they are indispensable for a safe and reliable operation. After this has been accomplished efforts must be made to develop suitable tests, which are as simple as possible, and can be quickly carried out, in order to fix and express these properties by certain values. It will serve the purpose best if these properties on which the quality of the oils is to be based are classified into commercial, operating and motor-technical data respectively, in order to follow a suggestion made by A. W. Schmidt.

A. *Commercial Data.*

1. *Flash point*; important for safety while storing and transporting.
2. *Content of water*; important for preventing corrosion during storage in tanks, etc.
3. *Purity* in respect to mechanical impurities as well as to compounds causing an objectionable odour or which are detrimental to health.

B. *Operating Data.*

1. *Solidifying point*; a characteristic for the flow of the oil by gravity, determining at the same time the temperature which will prevent the oil flowing from the tank of the vehicle to the feed-pump.
2. *Filtering ability*, particularly at low temperatures. This property is a characteristic for the flow of the oil through the filtering arrangements of the motor, which must always be present for protecting the pumping arrangements.
3. *Corrosion*; a guide for the chemical attacks on the metal walls of the storage tanks (zinc coating), tubes (copper pipes) and injecting arrangements.

C. *Motor-technical Data.*

1. *Viscosity*; a guide for the flowing and dispersing properties of the oil.
2. *Ignitability*; a characteristic of the oil for the starting and running of the engines.
3. *Coking properties*; a guide for the inclination of the fuel to carbonize around the inside of the nozzle.
4. *Calorific value*; a guide for the specific consumption and the efficiency of the oils.

* Paper presented for discussion at a meeting of The Institution of Petroleum Technologists and The Koninklijk Instituut van Ingenieurs at The Hague, 9th May, 1936.

5. *Efficiency on the smoking point*; a characteristic for the combustion property of the fuels.

Since reliable and approved testing methods are already available for the other properties, only the question of filtering quality, corrosion, ignitability, coking properties and the effect on the smoking point will

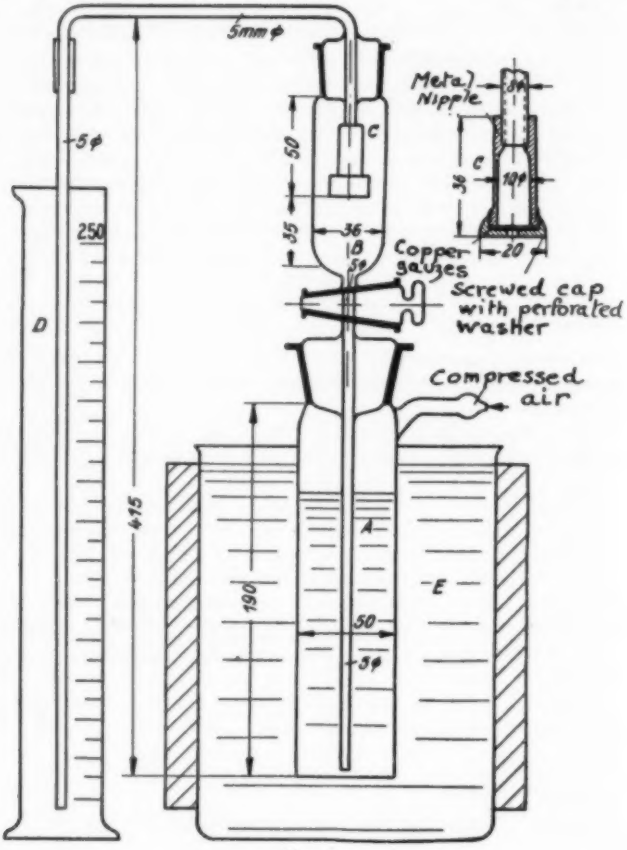

FIG. 1.

be taken into consideration. For the determination of these we have developed methods in closest contact with practical conditions, and by these methods have tested diesel oils having widely varying properties.

FILTERING ABILITY.

To determine the filtering ability of diesel oils we have developed a laboratory apparatus, as shown in Fig. 1. The apparatus consists of

three parts, which fit together by gas-tight ground surfaces, and it is provided with a pressure-resisting cock. The lower slender vessel serves to receive about 300 ml. of diesel oil. The middle portion of the apparatus is provided with a stop-cock carrying a cylindrical top piece, and to the central glass tube introduced into the top piece a brass socket is attached and fixed by cement. This funnel-shaped socket is provided with a hollow nut surrounding the end, and able to receive a set of washers of varying perforation and of copper gauzes having a certain width of mesh.

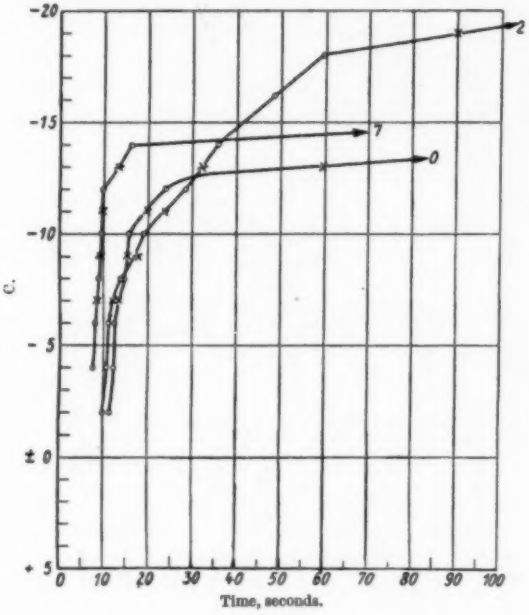

FIG. 2.

FILTERING ABILITY, I, GAS OILS.

Oil.	Turbidity point.	Solidifying point.
2	−6°	−18°
0	−6°	−14°
7	−8°	−14°

The filtering ability of an oil at a certain temperature is determined by means of this apparatus as follows :—

The diesel oil transferred into the lower vessel is cooled to the testing temperature by continuous stirring in a cooling bath containing alcohol and solid carbonic acid. The apparatus is then put together, and, the cock having been closed, compressed air is introduced at a pressure of 0·5 atmosphere. By careful opening of the cock the oil is allowed to rise just to the filtering level, and the cock is then again closed. The cock is again quickly opened, and at the same moment a stop-watch is started. The oil, being under vacuum, is now passing through the copper filter, and is

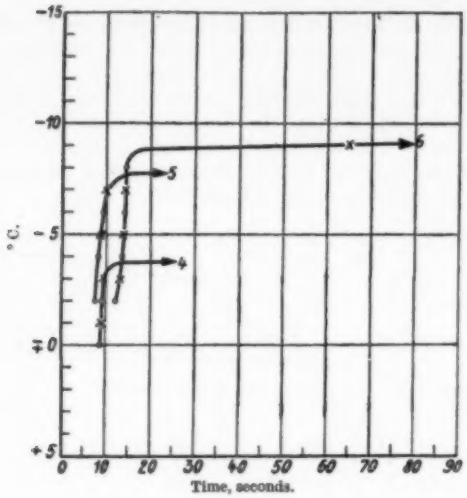

FIG. 3.

FILTERING ABILITY, II, GROUP A.

Oil.	Turbidity point.	Solidifying point.
6	−6°	−10°
4	−4°	−10°
5	−6°	−12°

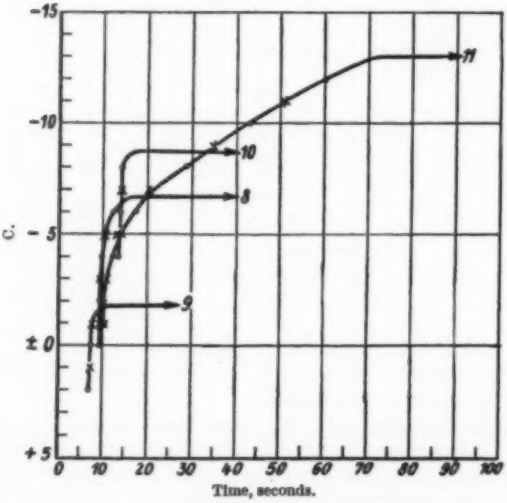

FIG. 4.

FILTERING ABILITY, III, GROUP B.

Oil.	Turbidity point.	Solidifying point.
8	−4°	− 8°
9	−2°	−12°
10	−7°	−11°
11	−3°	−14°

collected in a graduated measure. The time taken by the flow of 200 ml. of the oil represents a basis for estimating its filtering ability. Ten copper gauzes having 0·1 mm. width of mesh, equal to 3600 meshes per cm.^{2} are applied, and have a total filtering surface of 6 mm. After the test the filtering discs may be cleaned with benzole for further use.

By means of this apparatus numerous oils have been tested at varying temperatures, and Figs. 2–5 show the behaviour of the oils below the

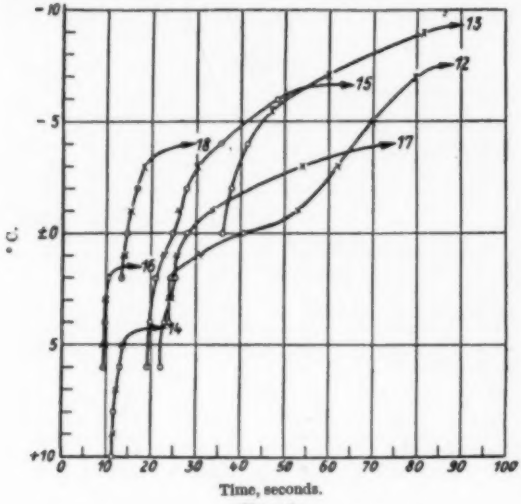

FIG. 5.

FILTERING ABILITY, IV, GROUP C.

Oil.	Turbidity point.	Solidifying point.
12	0°	−4°
13	−4°	−6°
14	+6°	−2°
15	+2°	−4°
16	+2°	0°
17	+2°	−4°
18	+2°	−6°

point of turbidity. The figures indicate that even oils having the same solidifying point show quite varying values as to their filtering ability at low temperatures. In the diagrams the times of flow in seconds are indicated in relation to the corresponding temperatures of the oils. The arrow indicates the temperature at which the filter is becoming obstructed or at which the filtering time is approaching the value ∞. The oils have each been tested first at temperatures of 0°, − 2°, − 4°, − 6° C. etc., and subsequently at − 1°, − 3°, − 5°, − 7° C. etc., showing an excellent conformity.

The brown coal-tar oils of the group C, being crude distillates of low-temperature tar, can in some cases be filtered at a temperature below their solidifying point, whilst with other oils an obstruction of the filter could be observed when the point of turbidity was approached.

As a value for the filtering ability, it is suggested to set up a so-called index of the filtering ability for a certain temperature, which can be deduced as a difference of time between the outflow of 200 ml. of oil on the apparatus mentioned with and without filter. By these means the effect of the flowing capacity of the oil will be excluded.

For our tests another type of apparatus, developed by Messrs. R. Bosch, was available, in which the arrangement for effecting the filtering process

TABLE I.

Corrosion.

Oil.	Creosote content, vol. %.	Neutralizing value.	Sulphur, %.	Corrosion.			
				Copper.		Zinc.	
				7 days, 20°.	24 hours, 50°.	7 days, 20°.	24 hours, 50°.
Diesel oil from petroleum							
1	1	0·09	0·82	0·4	0·4	0·4	0·2
2	0	0·52	0·25	0·4	0·3	0·7	0
3	0	0·44	0·36	0·5	0·7	0·4	0·1
Diesel oil from brown coal tar							
Group A							
4	0	0·03	0·80	0·5	1·2	0·8	0·1
5	0	0·17	1·34	0·4	0·2	0	0
6	2	0·03	1·28	0·4	0·9	0·2	0·1
7	0	0·03	0·23	0·4	0·4	0	0·2
Group B							
8	2	0·27	0·91	0·2	1·1	2·5	1·3
9	6	0·49	1·19	0·5	0·3	0	0·2
10	2	0·12	1·40	0·4	0	1·1	0·5
11	4	0·59	0·75	1·5	1·3	9·5	2·5
Group C							
12	0	0·47	1·00	0·8	0·8	1·7	0
13	10	0·88	0·85	0·4	2·5	10·0	10·5
14	0	0·18	1·57	0·6	0·3	0·5	0·2
15	4	0·04	1·34	0·2	0·7	3·0	1·2
16	6	0·69	0·83	2·3	6·6	14·0	7·2
17	10	0·49	0·86	4·5	2·6	11·2	2·8
18	9	1·19	0·77	4·2	5·6	15·4	4·4

scarcely differs from the actual operation in diesel engines. By means of a feed-pump driven by an electric motor, the oil coming from a tank is forced through a filtering cell applying a pressure of 0·5 atmosphere, and in this case the filter consists of the commonly applied felt pad. By means of this apparatus the filtering ability has been determined similarly as with the glass apparatus, determining the time of flow of 500 ml. oil at a certain temperature. Trials carried out in the cooled cell were qualitatively in satisfactory agreement with the determinations made in the laboratory. In each instance the critical temperature at which the oil is unable to penetrate the felt pad in sufficiently large a quantity could be ascertained with certainty by means of the laboratory apparatus.

Corrosion.

Suggestions applicable to the determination of the corrosive effects of diesel oils have so far not been published. We have been able to ascertain that between acid value, content of sulphur and of creosote on the one hand and of the inclination to corrosion of the diesel oils on the other, there exists no distinct relation (Table I). Since the sulphur in the form of aromatic compounds has no corrosive properties, the total contents of sulphur in the oil cannot be taken as a basis for valuing its good quality.

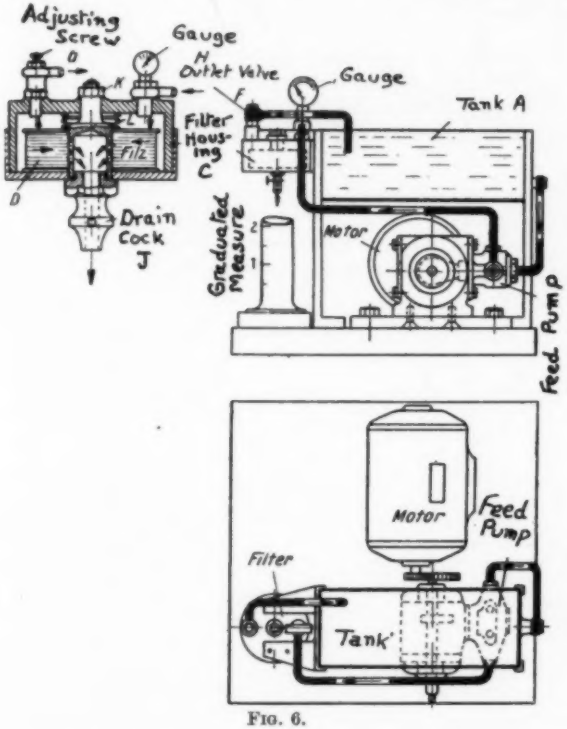

Fig. 6.

Under these conditions it was almost a necessity to determine the practical behaviour of the oil in contact with the different metals. While iron and aluminium react very slowly with diesel oils, even under accelerated conditions, copper and zinc are attacked. In the case of copper the chemical reactions take two directions. In one case the copper is dissolved as a metallic soap, by the contents of acid in the oils, and in the other the aliphatic sulphur reacts with the copper, forming copper sulphide. Thus in order to get a uniform indication of the corrosive attacks on copper, the following test has been applied :—

Strips of copper 10 by 100 mm. in size, having a thickness of 1 mm.,

are weighed and immersed in the oil to be tested, so that by using a test container of 25 ml. capacity 80 mm. of the strip are immersed in the oil. Before weighing, the strips are cleaned by the aid of fine steel wool. The

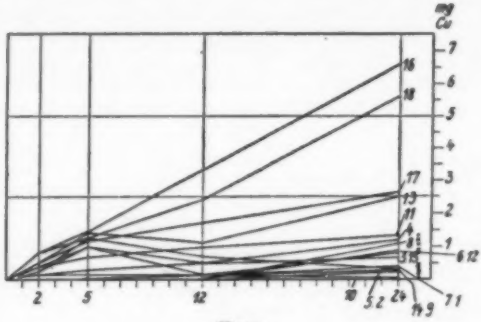

FIG. 7.

CORROSION.

Temperature of reaction, 50° C.

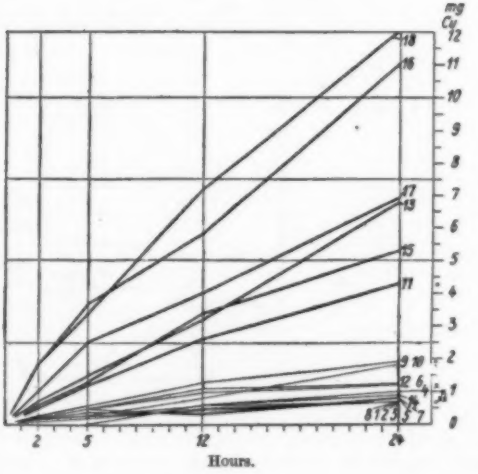

FIG. 8.

CORROSION.

Temperature of reaction, 75° C.

surfaces of the strips are slightly roughened. The oil is kept at a temperature of 50° C. for 24 hours. The strip is then withdrawn and cleaned by spraying it with a high volatile solvent (a mixture of even parts of benzole and ether). The strip is then dipped into a 10 per cent. solution of potassium cyanide, which, by forming a complex cupro-salt, causes the

copper sulphide which may cover the strip to dissolve. The strip of copper is washed by spraying it with alcohol, and again weighed. The loss of weight determined serves as a guide for the corrosive properties of the oil applied.

In the same manner, strips of zinc of equal dimensions are subjected to the diesel oil, and the loss of weight determined will furnish a second

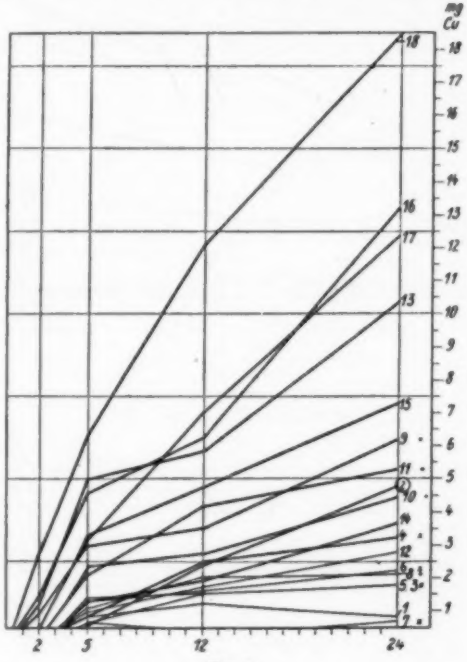

FIG. 9.

CORROSION.

Temperature of reaction, 100° C.

value, which particularly indicates the attacks of acids, since zinc is not affected by sulphur compounds, which at the same time cause the weight to increase.

In Figs. 7 to 12 the results of the tests of fifteen different oils are reproduced as graphs. These oils have been tested against copper and zinc at temperatures of 50°, 75° and 100° C. at time intervals of 2, 5, 12 and 24 hours in the same manner as indicated above. The verticals of the graphs represent the loss of weight in milligrams, whilst the horizontals correspond to the time during which the metal strips were subjected to the effect of the oils.

In Table I the different oils are compiled as to their contents of creosote and sulphur, including the neutralization value. At the same time, the

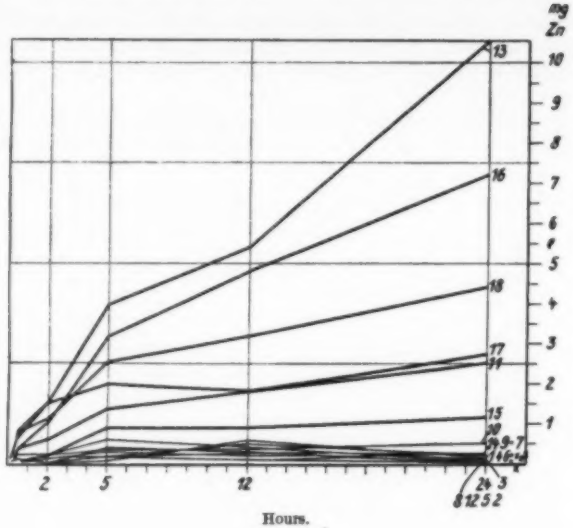

FIG. 10.
CORROSION.
Temperature of reaction, 50° C.

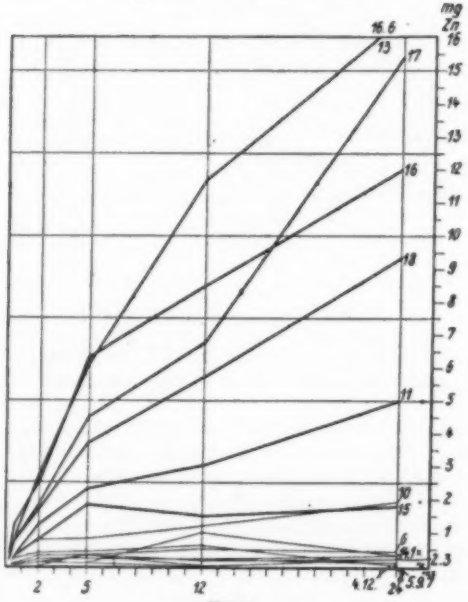

FIG. 11.
CORROSION.
Temperature of reaction, 75° C.

attack (corresponding to the loss of weight) on copper and zinc by the effect of the oils is stated for a time of 7 days at room temperature of the oil, as well as for 24 hours at 50° C. oil temperature. From these results it can be deduced that the tests carried out at room temperature and those covering a shorter time are qualitatively in good agreement. It will be further noted that oil No. 13 attacks copper at 50° C. much

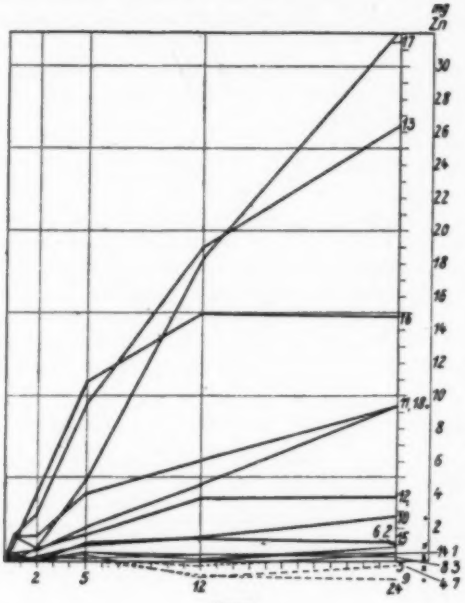

FIG. 12.

CORROSION.

Temperature of reaction, 100° C.

more strongly than at room temperature, and this can be explained by the acid quality of the oil, which shows its effect against zinc quite distinctly already at 20° C.

It does not appear to be advisable to raise the temperature of the oil beyond 50° C. for the short-time tests, since at higher temperatures the corrosive attacks on the metals are not in proper relation to practical conditions. As indicated in Fig. 9, even good diesel oils (oil No. 2) produced from crude mineral oil considerably attack copper at 100° C.

The test suggested should be suitable for the recognition with certainty of corrosive oils, and, on the other hand, it will avoid an unjustified and too sharp judgment of diesel oils.

IGNITABILITY.

By means of chemical or physical tests, the ignitability of diesel oils

cannot be determined with certainty. Neither the determinations of the ignition point in a crucible or pressure bomb, nor physical values like diesel index, surface tension, density, boiling-point value, etc., are absolutely reliable as a basis for the ignitability of diesel oils.

We have given preference to the testing of diesel oils by means of an engine, and in the choice of the testing method and of the testing engine we have principally been guided by the following conclusions :—

1. Application of a type of engine built in series and obtainable at low costs.
2. Application of a type of engine with as low a capacity as possible, so as to keep testing expenses at a low rate.
3. Greatest simplicity of supervision.
4. Good repeatability of results.
5. Easy transfer of the results and ready observation of the behaviour of the oils in the operation of the engine.
6. Exclusion of irregularities due to the formation of residual coke in the combustion space, particularly on or inside the nozzle, and, on the other hand, by an alteration of the combustion space volume (variable compression) causing altered conditions of injection.

For testing the ignitability of diesel oils a single-cylinder diesel engine was used, which was constructed by the Motorenfabrik Deutz and supplemented by Messrs. Bosch with the necessary pumps and testing arrangements :—

Volume of stroke	1·92 litres
Compression	1 : 14·5
Revs. per min.	1,100
Normal capacity	about 13 H.P.
Oil feed	direct stream injection
Bosch pump with nozzle, having three holes of a width of 0·25 mm.	
Angle of injection	50°
Injection point about 30° crank angle before upper dead centre	
Quantity of oil	about 140 mm.³ per stroke
Nozzle pressure	about 100 atmospheres.

The well-known so-called starting and throttling method is used, the engine being driven by an outside source of power and the speed maintained at 1000 revolutions per minute. By means of a butterfly valve the volume of air drawn in is varied. The vacuum created by throttling the valve in the suction tube is a basis for the ignitability. The higher the vacuum reached, expressed in mm. mercury, at which the oil will still ignite, the better is its ignitability.

As to the scale for valuing the ignitability, we have retained the cetene value, and apply as relative starting and finishing points mixtures of cetene and α-methylnaphthalene. It must here be pointed out that cetene does not maintain its quality during storage if air is in contact with it, and this has also been ascertained by other observers.

The ignitability of an oil is very much affected by the temperature of the air drawn in, as well as by the temperature of the cooling water, as can be noted from Fig. 13. In the method suggested by us the air drawn in, as well as the cooling water, are maintained at a temperature of 45° C. These conditions can also be complied with on hot summer days without difficulty, and the engine will be able to test oils having cetene values

varying between 30 and 70. Quite apart from the fact that we consider this range quite sufficient, it should here be mentioned that by lowering or raising the temperatures of air and cooling water higher or lower cetene values may also be determined.

The testing of the oils is effected as follows: After adjusting the engine to the standard operating conditions in respect to speed, temperature of air and cooling water, the oil contained in a small vessel is injected into

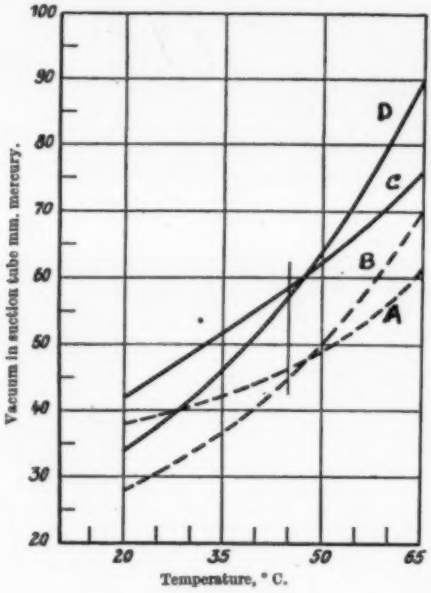

FIG. 13.

EFFECT OF AIR TEMPERATURE AND COOLING WATER UPON THE IGNITABILITY OF DIESEL OILS.

A. Oil A, air, 45° C.
B. „ A, water, 45° C.
C. „ B, air, 45° C.
D. „ B, water, 45° C.

the explosion chamber by touching a key which electromagnetically effects the injection. By a step-like throttling of the air drawn in, it is noted where the first misfiring occurs, which can be observed readily by the formation of oil fog in the exhaust pipe, and also by the ear. In order to determine exactly the critical value—viz. the so-called starting value—an injection must be effected at intervals of 10 seconds, to be able to ascertain without any doubt whether with ten injections an ignition has taken place each time. The starting value is correct if by the least further throttling of the air the misfiring is observed.

The engine used for the tests is reproduced in Figs. 14 and 15, and Figs. 16, 17 and 18 show the gauge curves of the engine. In Table II

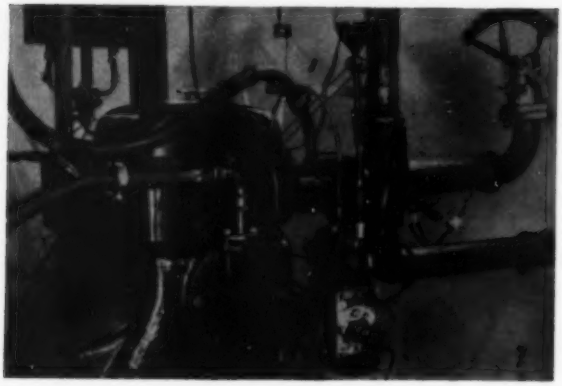

FIG. 14.

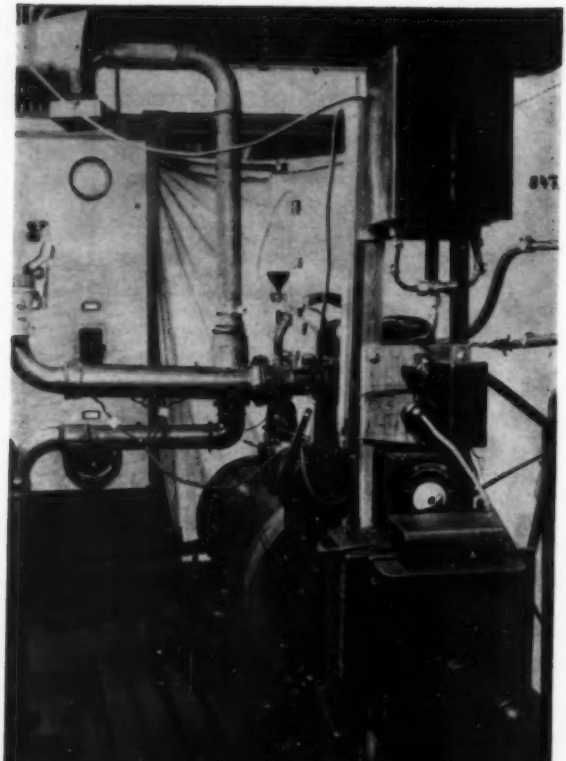

FIG. 15.

cetene values of different oils are given which have been determined by the aid of this engine.

To make it clear how the values of ignitability determined correspond with those obtained with other testing engines, particularly with the C.F.R. engine, or, in other words, how far it should be possible to reduce the differences of testing results caused by mechanical effects of the engine,

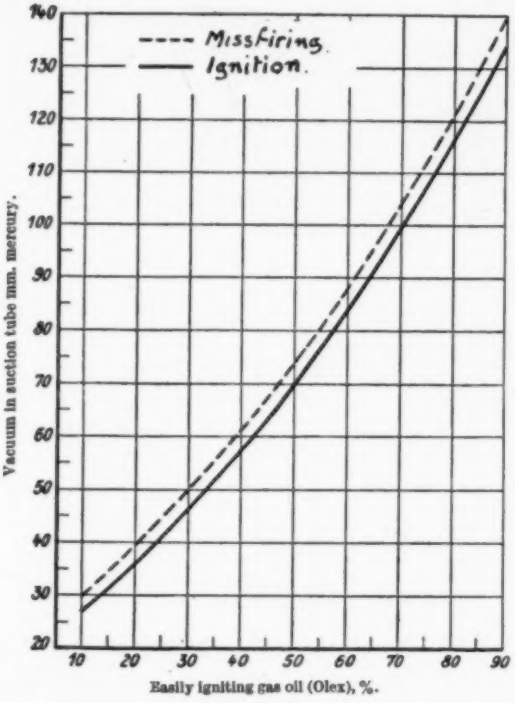

FIG. 16.

we have carried out corresponding tests with the same oils in different places. From Table III it will be deduced that with small differences corresponding results are obtainable.

COKING PROPERTIES.

It is well known that some diesel oils have an inclination to carbonize around and inside the nozzle. This process is effected by the raised temperature of the nozzle and by a thermal decomposition of the oils, and may cause very serious interruptions with the injecting arrangement. In order to test this tendency to carbonize of diesel oils, the tests by Muck or Finkener have been applied, or the Conradson test adapted in the U.S.A., or the method introduced by Ramsbottom in England.

It is known that particularly the three first-mentioned methods show large variations in their results, because the conditions of operating the test, particularly the temperature applied, cannot be evenly maintained. The diesel oils have a widely varying curve of boiling points, and this makes it very difficult to subject the oil in the crucibles to an even heat.

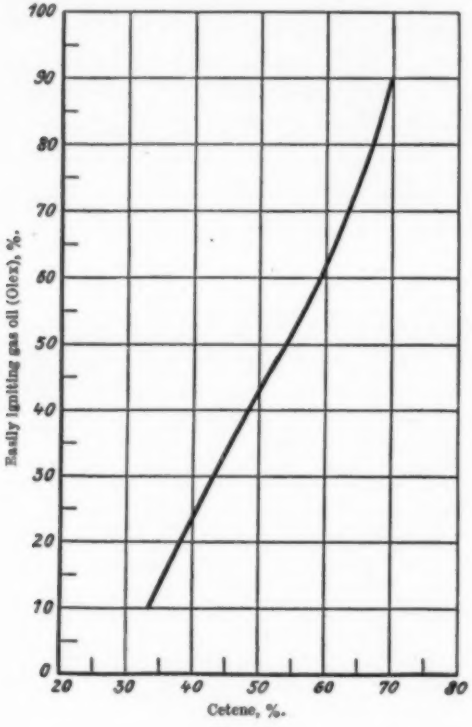

FIG. 17.

These testing methods may have proved their applicability for lubricating oils, but not for diesel oils.

Our objections against the application of these methods are based principally on the fact that the carbonization of the oil on and inside the nozzle takes place under considerably differing conditions. All the laboratory methods mentioned have in common the total volatilizing of the oil, whilst in the case of the carbonization in the nozzle a temperature of 180° C. is scarcely exceeded.

In order to approach operating conditions of diesel engines as closely as possible, we suggest the following method to determine the tendency to carbonize of diesel oils.

Five grams of oil are weighed into a small beaker, and the latter is placed inside a pressure bomb, as shown in Fig. 19. Into this bomb,

which is provided with two needle valves (*e*, *d*), compressed air is introduced until the pointer on the gauge (*k*) indicates a pressure of 20 atmospheres. The bomb is then heated for 2 hours in a metal bath (*m*), which by automatic adjustment maintains the temperature evenly at 155° C.

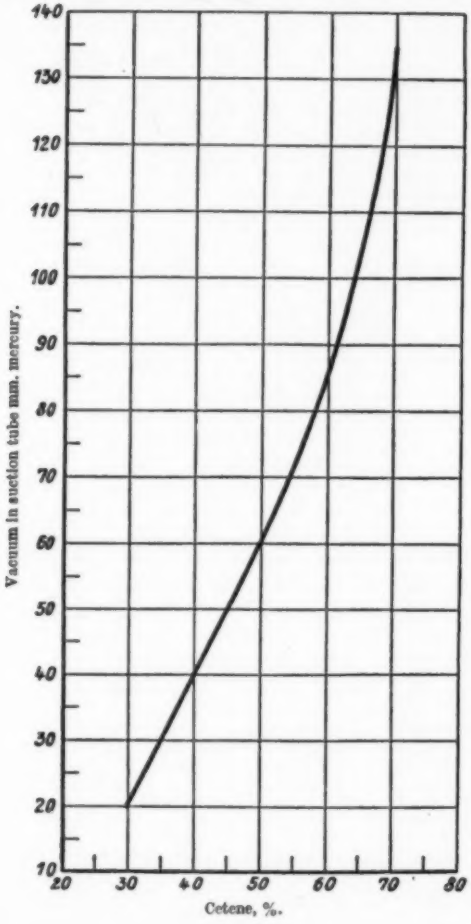

FIG. 18.

After cooling of the bomb, the beaker is removed and the oil is tested as to its contents of asphalt and coke by the well-known methods applied for lubricating oil.

In Table IV the results of tests of eighteen different oils are given.

While the gas oils No. 2 and 3 form only very small amounts of asphalt and coke, the residue not soluble in normal benzine is very large in the gas

oil No. 1 produced by cracking. Of the brown coal-tar oils, the highly refined oils of group A show the least inclination to form asphalt and coke.

TABLE II.

Ignitability (Army Diesel Testing Engine.)

Oil.	Starting value (mm. Hg.)	Cetene value.
Diesel oil from petroleum		
1	42	41
2	120	67·5
Diesel oil from brown coal tar		
Group A		
4	45	42·5
5	58	49
6	46	43
Group B		
8	54	47
9	52	46
10	44	42
11	50	45
Group C		
12	50	45
13	34	37·5
14	44	42
15	42	41
16	52	46
17	40	40
18	40	40

Responsible for the formation of asphalt and coke will be in the first place unsaturated and oxygen compounds, and from Table IV it can be deduced

TABLE III.

Ignitability (Centene Values.)

Test No.	I Gardner-Engine (Körting-Engine.)	II DVL-Single-Cylinder Engine.	III C.F.R.-Engine.	IV C.F.R.-Engine.	V Army Diesel Testing Engine.
1	30·5	33	36	36·5	36
2	40	40·5	42·5	43·5	41
3	50·5	48·5	51·5	52	50
4	59	57·5	61	61·5	59·5
5	70·5	69·5	76	70	68·5
6	35	35	38	40	41
7	64·5	62·5	66	61·5	66
8	41	40	43	45·5	43
9	74	85	82·5	77·5	< 70
10	44	39	43	44·5	42

that the creosotes principally participate in the formation of asphalt. As indicated by the behaviour of oil No. 13, the nature of the creosotes contained in the oil will have a decisive effect.

The testing method suggested has the main advantage that overheating of the oils is prevented, and the operation of the test is outlined so clearly that it may be repeated several times with corresponding results. As to the limits of exactness of this method, the parallel tests compiled in Table V will allow a judgment.

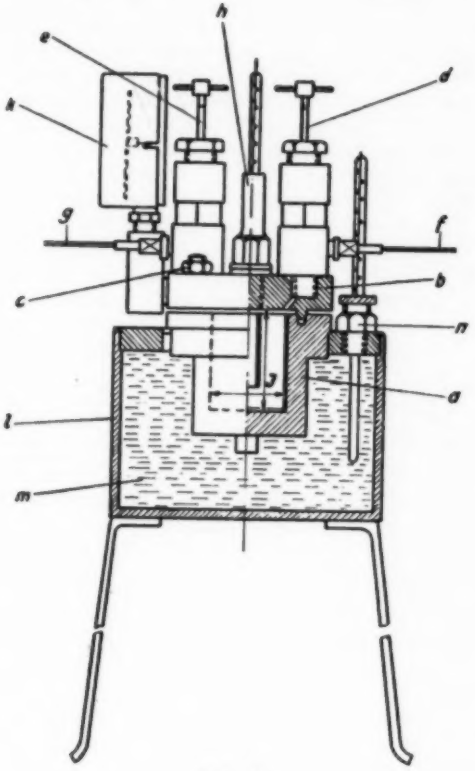

FIG. 19.

EFFECT ON THE SMOKING POINT.

Ignitability and carbonizing properties do not suffice to judge the qualities of a diesel oil. With a faultless ignition the kind of combustion or its speed is of great importance for the operation of the diesel engine. On this depends:

1. The formation of asphalt, coke and soot which will lead to deposits in the combustion chamber and contaminate the diesel oil, and may cause very serious difficulties.

2. The effect of the motor which is being reached when operating with smokeless combustion.

TABLE IV.

Tendency to Carbonize.

Oil.	Insoluble in Normal Benzine, %.	Hard Asphalt, %.	Coke, %.	Creosote Content, vol. %.
Diesel oil from petroleum				
1	4·5	2·5	2·0	1
2	0·13	0·02	0·11	0
3	0·13	0·04	0·09	0
Diesel oil from brown coal tar				
Group A				
4	1·7	1·2	0·5	0
5	1·6	0·7	0·9	0
6	3·1	2·0	1·1	2
7	0·09	0·01	0·08	0
Group B				
8	4·2	2·4	1·8	2
9	5·3	4·0	1·3	6
10	5·9	3·5	2·4	2
11	5·3	3·4	1·9	4
Group C				
12	5·9	4·5	1·4	0
13	5·3	4·7	0·6	10
14	1·8	0·7	1·1	0
15	8·2	6·3	1·9	4
16	6·9	5·6	1·3	6
17	12·5	11·4	1·1	10
18	8·6	7·7	0·9	9

The more the oil is inclined to form asphalt, coke and soot, the less oil can be injected, and the effect of the engine is consequently reduced.

This question is of considerable importance for the automotive appli-

TABLE V.

Tendency to Carbonize (Comparative Tests).

Oil.	Insoluble Normal in Benzine, %.	Hard Asphalt, %.	Coke, %.
4	2·1 1·7	1·6 1·2	0·5 0·5
5	1·6 2·1	0·7 0·7	0·9 1·4
7	0·09 0·11	0·01 0·02	0·08 0·09
8	4·2 4·1	2·4 2·6	1·8 1·5
9	5·3 5·6	4·0 4·3	1·3 1·3
14	1·8 2·4	0·7 1·5	1·1 0·9

cation of the diesel engine, and special attention must be paid to it if automotive diesel engines are to enjoy a further wide introduction.

The determination of the effect on the smoking point is already considered of great importance by the diesel-engine constructors, and this property is also taken into account for judging a diesel engine having to consume a certain oil. On the other hand, the quality of a diesel oil is valued by testing it in this respect in an available engine.

The difficulty connected with this test rests with the proper and correct determination of the smoking point. Our efforts are directed to test the exhaust gases by means of a photo-electric arrangement, and it must thereby be considered that particles of soot as well as foggy constituents appear side by side, but react in quite a different manner on the photo cell. These last circumstances have made it so far very difficult to reach an irreproachable value for the smoking point. The development in this connection is still pending, and has not been concluded, on account of the difficulties mentioned. A report about this work will be published at a later date. We are, however, justified to hope that before long we shall be able to reach a method for the physical analysis of the exhaust gases.

Conclusions.

The testing methods suggested above have been developed in closest contact with the experiences gained in practical operation. In view of this aim, means and ways had to be adopted which purposely differed from the well-known chemical methods generally applied for testing mineral oils.

It will be understood that our work has not been concluded, and in connection with the most important points numerous tests must still be carried out.

As to the question of corrosion, the effects of the flow of the oils must be studied, as well as the effects of the oxygen and the humidity of the air. In these tests numerous metals and metal alloys must be included.

For the practical use of the method for testing the carbonization properties of the oils it is decisive to know what connections exist with operating conditions. At present trials have commenced to throw light on the formation of coke within and around the nozzle. For this purpose a continuous run is applied, as well as different shapes of nozzles, while the temperatures of the nozzles are also varied. For this work diesel engines with direct injection are given preference. Only after the conclusion of these tests will it be possible to judge the practical value of the suggested laboratory work, and to approach the setting up of standards for the respective limits.

The most prominent advantage of the new testing methods rests with the fact that there now exists a possibility to express in fixed values for the practical properties which are demanded from diesel oils. Such limit values do not represent absolute figures, since they must be adjusted at times in accordance with the developments taking place in the constructional technics, as well as in the chemistry of oils. The manufacturer of diesel oils is now in a position to form an opinion as to the quality of his

products by means of these short-time tests, and the works producing automotive engine constructions are able to look out for better solutions and more favourable conditions, whilst the consumer can guard himself by testing against unsuitable diesel oils, and is thus protected against stoppages. It is thus really necessary that these testing methods are generally applied, so that the quality of the diesel oils will be judged by these testing methods and their value be based on their results.

Testing Methods.

(A) *Determination of Filtering Ability of Diesel Oils.*

The diesel oil to be tested is passed through a large folded filter at room temperature, and thus freed from water and solid impurities kept in suspension.

300 ml. of the filtered oil are transferred into the lower slender portion of the laboratory apparatus. The vessel rests in a large cooling bath of alcohol, and by means of a clamp on the neck is kept in position. While the oil is kept continually in motion by stirring with a thermometer, the bath is cooled gradually, by adding dry ice (solid CO_2), to the testing temperature at which the filtering ability is intended to be determined. After the oil has reached this temperature, the thermometer is withdrawn and the middle piece, provided with a stop-cock, is placed in position. At the same time the upper part is placed into the ground neck of the middle piece after the nut has been screwed on to the brass tube holding a brass washer having an open width of 6 mm. and ten good copper gauzes having a width of mesh of 0·1 mm. Now three strong springs are fixed round a ring held by a stand, and these are tightly connected to the upper portion of the apparatus, so that its top cannot give way in an upward direction.

While the cock is closed, air is introduced through the side branch of the lower vessel at a pressure of 0·5 atmosphere, and by a rapid short opening of the cock the surface of the oil is forced down below the metal nipple. The cock is then opened with a jerk, at the same time starting a stop-watch.

The time (expressed in seconds) which is required for 200 ml. of the oil to be transferred into a measuring vessel is determined. To prevent a frothing of the outflowing oil, the latter is allowed to pass through a long glass tube reaching down nearly to the bottom of the measuring cylinder. The volume of oil displaced by this glass tube must naturally be taken into account when gauging the cylinder.

If the diesel oil flows very slowly through the gauze filter on account of heavy discharges, *i.e.* taking more than 90 seconds, or if a complete obstruction of the filter occurs, the value ∞ is to be taken as the time of flow.

After the test the pressure-tight connection is loosened by removing the springs, the gauzes are withdrawn, and after they have been washed with a mixture of benzole and ether (1 : 1) they are dried in a current of air.

The nut and the washer are replaced without inserting the gauzes. The diesel oil contained in the measuring vessel is re-introduced into the lower slender portion, and by means of the cooling bath is again cooled down to the previous testing temperature. The time of flow of 200 ml. of oil

is again determined in the same manner without the gauzes, as stated before. The difference between the two outflowing times determined serves as a value for the filtering ability of the diesel oil at the chosen temperature (" Index of filtering ability ").

It should be pointed out particularly that it is no use to accelerate the adjustment of the temperature of the oil by allowing the temperature of the cooling bath to fall considerably below the testing temperature of the oil, because this will lead to incorrect results of the filtering ability.

(B) *Test of the Corroding Properties of Diesel Oils.*

A strip of copper 100 by 10 mm. and 1 mm. thick is cleaned and slightly roughened by means of fine steel wool. The strip is weighed and immersed into the diesel oil contained in a measuring cylinder of about 100 mm. height and 20 mm. internal diameter, having a capacity of 25 ml., so that 80 mm. of the strip are immersed in the oil. At the same time a strip of zinc of equal dimensions, and having been subjected to the same preliminary treatment by means of steel wool, is immersed in the same manner in a measuring cylinder containing oil of the same sample. These measuring cylinders are conveniently placed for 24 hours into a drying cupboard, the temperature of the latter being kept constantly at 50° C.

After this time has elapsed the cylinders are withdrawn and the strips are cleaned by the aid of a wash-bottle containing a volatile solvent (a mixture of benzole and ether 1 : 1).

The copper strip is immersed into a 10 per cent. solution of potassium cyanide until its dark skin (copper sulphide) has been dissolved. The strip of copper is now cleaned by the aid of a wash-bottle, first with water, and subsequently with absolute alcohol, and again weighed.

The strip of zinc, after having been washed in the same manner with the mixture of benzole and ether to remove the oil covering the surfaces, is also weighed.

The loss of weight of the strips of copper and zinc respectively expressed in milligrams serves as a value for the corroding properties of the diesel oil tested.

(C) *Test for the Tendency to Carbonize of Diesel Oils.*

For testing the tendency to carbonize or the carbonizing properties of diesel oils, a pressure bomb made of non-rusting chromium nickel steel is used. The bomb is provided with two needle valves and a certified pressure gauge, as well as capillary connecting tubes.

The pressure bomb is heated by a Wood's alloy-bath, the temperature of which is automatically adjusted by means of a gas relay and a " Vertex " contact thermometer (having a range of temperature from 50 to 250° C.), a bunsen burner completing the outfit.

Five grams of the diesel oil to be tested are weighed into a glass beaker which has a height of 55 mm. and an internal diameter of 27 mm. The beaker is placed into the bomb in such a manner that the bulb of the thermometer in the lid of the bomb reaches into the oil. Care must be taken that the bulb of the thermometer does not break the beaker. After the lid of the bomb has been tightened by screwing down the nuts, the bomb is slowly filled with air, applying a pressure of 20 atmospheres. It

is advisable to take a safety gauge into the circuit (as used in connection with a calorimeter bomb), which blows off if a pressure of 30 atmospheres is reached. The bomb is now placed into the metal bath, which has been heated by means of the bunsen burner to a temperature of 150° C. The temperature of the bath is maintained constant at 155° C. The time when the bomb is being placed into the bath always counts as the commencement of the test. After exactly 2 hours the bomb is lifted out of the bath and allowed to rest for 1 hour at room temperature. After the pressure has been released gently, the lid of the bomb is removed carefully and the contents of the beaker are washed into a 300-ml. Erlenmeyer flask with ground stopper. The inner surface of the lid and the glass wall are thoroughly cleaned. 200 ml. normal benzine (Schering-Kahlbaum) serve as a solvent.

After standing for 24 hours, the clear solution in which the insoluble matter has settled down can be filtered through a porcelain filtering crucible without difficulty. The residue in the crucible is freed from oil by washing with normal benzine. After drying for 1 hour at 105° C. and cooling in a desiccator until the thermometer of the latter indicates room temperature, the residue is weighed, and subsequently the hard asphalt is dissolved in hot benzole. After drying and cooling the crucible is again weighed.

The values thus determined—viz. substance insoluble in benzine, substance soluble in benzole (hard asphalt) and residual matter (coke)—are expressed in per cent. by weight, and calculated in relation to the amount of oil used for the test.

(D) *Determination of Ignitability (Cetene Values) of Diesel Oils.*

The army testing engine is being supplied together with a three-phase electric motor serving as source of power for driving the engine. When ordering the set, the kind of current available on the testing station must be stated.

The testing engine is first operated for about 1 hour at 1,000 revolutions per minute, driven by the electric motor, to balance its action and to warm the cooling water. After the prescribed operating conditions as regards revolutions, (n = 1,000) temperature of air sucked in and cooling water (45° C.) are maintained, the testing of the diesel oils can be commenced. While the temperature of the air sucked in is being adjusted automatically, the temperature of the cooling water must be adjusted by a corresponding addition of fresh water by means of a regulating cock.

The small reservoir arranged above the injection pump is being filled with the diesel oil to be tested, and if necessary the tube leading to the injection pump must be well flushed with the oil up to the injecting nozzle. By operating the key—at first with the throttle valve fully opened—oil is once introduced into the combustion space. While throttling the air drawn in step-like, it must be determined at what point the mixture fails to ignite, and this can be observed by the naked eye by the formation of an oil fog in the exhaust pipe, and also by the ear. By these means the highest value of suction is determined at which an ignition of the oil takes place in each case. This suction, indicated by the mercury gauge connected to the set, is correct if by the least further throttling of the air

drawn in the ignition of the oil is observed to fail. To determine exactly the critical value—the so-called suction value—an injection is effected ten times at intervals of 10 seconds, and in each instance an ignition must be observed.

It is certain that before testing diesel oils the motor must be gauged. In order to save the expensive cetene, the routine control of the engine is carried out by using comparative oils (sub-standards), Abadan and S 300 as supplied by the Olex Company. If once the starting values of the different mixtures of cetene and α-methylnaphthalene have been determined and these values have been plotted down to correspond with those of different mixtures of the sub-standards, by means of this gauging curve, the ignitability of the diesel oils to be tested can always be expressed in cetene values. The exactness of this testing method can, under these assumptions, be controlled by checking with sub-standards of known ignitability from the Olex Company.

As a lubricating oil for the engine the Gargoyle AF supplied by the "Deutsche Vakuum A.G." has been used.

SPECIFIC REFRACTIVITY.

I.P.T. Serial Designation—L.O. 41.

Definition.

Specific refractivity is defined as $R = \frac{n-1}{d}$

where n = refractive index for D line (sodium light),
d = density in gm./ml.

Both n and d should be determined at the same temperature, preferably at 20° C.

Sampling.

It is essential that a sample to be used for the determination of physical constants should be obtained in strict accordance with the prescriptions laid down in "Standard Methods for Testing Petroleum and Its Products."

Special attention is directed to the precautions therein recommended to ensure that the sample be uncontaminated by foreign substances such as zinc chloride from the soldering flux used in tin can manufacture, coal-tar products from the paint used for painting drums or from the sealing compounds commonly employed for closing the seams of such drums. It is further recommended that the final samples for testing be preserved in glass-stoppered bottles, since it is known that resinous substances liable to affect the physical constants are readily dissolved and extracted by the oil from ordinary corks, and this source of contamination is accentuated if the latter have been coated with sealing wax.

Determination of Refractive Index.

Refractive Index shall be given for sodium light.

Any form of refractometer may be employed providing that it is capable of giving results to an accuracy of ± 0·0005.

It is recommended that the instrument be calibrated, and periodically checked, with liquids of known refractive index, such as carbon tetrachloride R.I. and benzene R.I.

Special care must be taken that the temperature of the sample is controlled to ± 0·5° C. of the adopted temperature.

Density.

The density shall be determined by means of a pyknometer or bottle having a minimum capacity of 10 ml. or by a *density* hydrometer. If the latter is employed it shall conform to the British Standard Specification No. Ia or IIa.

The density shall be expressed in grams per millilitre at 20° C. and shall be determined correct to ± 0·0005 gm./ml.

Care must be taken that the thermometers employed are accurate to within ± 0·1° C.

It should be noted that specific gravity at 60° F./60° F. cannot be correlated with density at 20° C. without an accurate knowledge of the oil concerned, and that the denominator in the formula for specific refractivity is density and *not* specific gravity.

Accuracy.

Provided that all the above precautions are faithfully observed, the specific refractivity can be determined to an accuracy of ± 0·001.

Copies of the above can be obtained on application to the Secretary of the Institution.

THE ADSORPTION OF BITUMEN AND ITS CONSTITUENTS BY CERTAIN NATURAL AND TREATED EARTHS.*

By H. T. Lorne, A.R.C.S., B.Sc. (Student Member).

SYNOPSIS.

The relative influence of the adsorbent capacity and the surface area per unit volume with reference to the "efficiency" of fillers is discussed. The effect of time on the adsorption in A.C.'s; the significance of the temperature of activation of some fillers. A distinction between adsorbents and absorbents is emphasized.

A comparison between the earths as bleachers of solutions of oil and of bitumen is made. The extraction of epuré filler and an observation.

Dry limestone as a decolorizer of bitumen solutions and of asphaltic crudes; oil migration.

Experiments have been carried out to calculate the percentage of irreversible adsorption that takes place when decolorizing tests are performed on solutions of bitumen, asphaltenes, and resins and inert oils in carbon disulphide. By analyses of exhaustive extracts and of direct filtrates it is possible to deduce the type of reaction that takes place and consequently how an earth decolorizes.

An attempt has been made to find what chemical reaction (polymerization, etc.) takes place during the adsorption by active earths of resins derived from a residual petroleum bitumen.

Introduction.

The researches of A. Evans [1, 2] have shown that the properties of asphaltic cements (*i.e.*, mixtures of asphaltic bitumen † and finely divided solids or "fillers") vary considerably with the type of filler in question, when comparing cements of equal filler content. This paper is in no way devoted entirely to an attempt to arrive at conclusions as to the causes of the phenomenon, but a certain amount of light is thrown on the problem by a study of the adsorbent action of these fillers. The work of Neumann,[3] Wilhelmi,[4] and others on certain earths has been devoted largely to theoretical considerations of their total surface areas per unit volume. Actually the surface area, in many cases at least, may differ widely from the theoretically calculated values, and despite much work on the subject carried out in various branches of science,[5, 6] it would appear that there is no accurate method yet available for measuring the surface area of finely divided solids.

Generally, as can be expected, the greater the surface area of a filler per unit weight, the higher the melting point and mechanical strength of the asphaltic cements composed of a given proportion of the same asphaltic bitumen. The investigations of Evans and others have shown that another important factor, not necessarily related to the total superficial area of the filler per unit weight, must be considered.

* Paper awarded Students Medal and Prize, 1935.

† Hereafter the term "bitumen" is used to represent "asphaltic bitumen."

Among the fillers that have been examined to date, only two—namely, Florida earth and activated bauxite—have been widely recognized as decolorising adsorbents and used as such in the oil industry. Owing to their relatively high cost, fuller's earth and other adsorbent powders (with the exception of the natural filler already present in Trinidad Lake Asphalt) have not been used hitherto as fillers in the asphalt industry; but since it has been suggested that the partial replacement of the cheaper fillers by adsorbent earths might improve the quality of asphalts, the determination of the relative "efficiency" of some of the better known finely divided adsorbents is of considerable practical importance. An attempt has been made to determine what relationship exists between the decolorizing powers of such earths and their "efficiency" as fillers. (By the term "efficiency" is meant the power of increasing the melting point and hardness of a bitumen by the addition of a certain proportion of filler without at the same time rendering the mixture unduly dry and brittle.)

Another problem of no little importance concerns the efficiency of fillers which are not necessarily *ad*sorptive in action, but in which the cellular structure of the individual particles causes a considerable amount of *ab*sorption to take place.

Experimental.

As a basis of investigation, routine experiments were carried out by the author on cements composed of a typical residual petroleum bitumen and certain selected earths. The bitumen used was a commercial product known as "Mexphalte" "E" Grade, having the following physical properties:

Melting point (Ring and Ball) 57° C.
Penetration at 25° C. (100 gms., 5 secs.) 48 units.
Ductility at 25° C. (5 cm. per min.) greater than 100 cm.

The earths selected included:

(1) *Florida earth.*—This extremely active natural fuller's earth is used on the most varied of petroleum products, ranging from the light kerosines to the waxes and dark cylinder oils. The finely divided variety which is suitable for use in the contact process was selected. A screening analysis showed that practically all the earth passed the 200 mesh B.S.I. sieve.

(2) *Bauxite*: A fine-grade Indian variety was used. This earth is noted for its desulphurizing properties,[7] but its application has been largely limited to the lighter petroleum distillates and to paraffin wax.[8]

The mechanical analysis was as follows:

Retained on the 50-mesh screen	28·6%
Passing 50, retained on 80-mesh-screen	26·9%
„ 80, „ 120 „	8·8%
„ 120, „ 200 „	18·4%
„ 200	17·3%
	100·0%

(3) *Kieselguhr or diatomite.*—Although only a poor decolorizer, this earth was selected for its absorbent properties.[9, 10]

(4) *Terrana earth.*—By virtue of an acid treatment, this Bavarian clay

is claimed to have certain superior properties, especially in connection with acid-treated oils. 90 per cent. passes the 200-mesh sieve.

(5) *Fuller's earth.*—The "XL" grade of the well-known fuller's earth mined at Redhill was selected. This adsorbent has been dried and finely ground, but not otherwise treated. It was anticipated at the time that since it is only a moderate decolorizer for petroleum products, it would prove also to be inferior to the more efficient oil decolorizers when used as a filler.

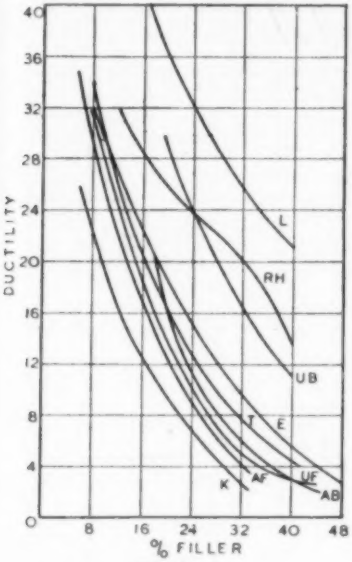

FIG. 1.

L, Limestone.
RH, Fuller's earth.
AB, Activated bauxite.
UB, Unactivated bauxite.
E, Epuré.

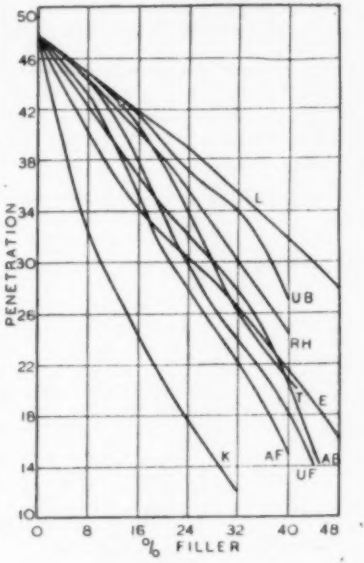

FIG. 2.

AF, Activated Florida.
UF, Unactivated Florida.
T, Terrana.
K, Kieselguhr.

(6) *Limestone.*—Although not an adsorbent material, this powdered Mendip limestone was included because it is a filler commonly used in making asphaltic cements, and in order, if possible, to throw some light on certain problems connected with oil migration. All the limestone passed the 120-mesh sieve.

Observing all the necessary precautions, the mixing of the bitumen and filler was carried out by a method very similar to that described by Evans.[1] Only small quantities (*ca.* 200 gms.) were experimented with. After filling suitable moulds with the hot A.C., and allowing to cool under the standard conditions laid down in the I.P.T. Standard Methods Book, the following three tests were made :

(1) Melting point by the Ring and Ball method.
(2) Ductility at 25° C. (Fig. 1).
(3) Penetration at 25° C. (Fig. 2).

If the ductility of any cement is plotted against its melting point, curves similar to those in Fig. 3 may be obtained.

From this, the rough working rule may be deduced that in the case of the majority of fillers of good "efficiency," cements of the same ductility have approximately the same softening point. It must be emphasized, though, that this rule is only approximate, and is brought out by fillers of higher "efficiency."

The magnitude of the effect of the addition of kieselguhr to bitumen is extraordinarily high. That this is so is not altogether surprising when one takes into account its very low apparent specific gravity and the enormous

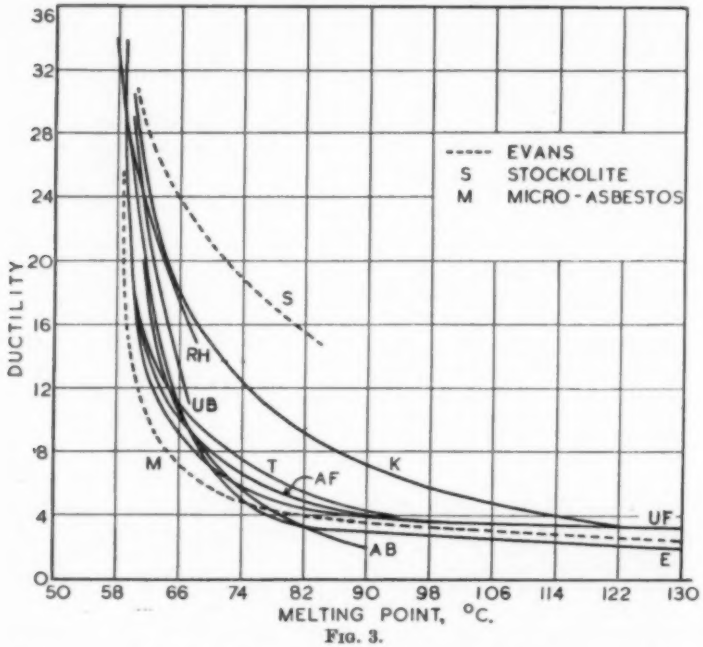

FIG. 3.

surface area available.[10] The true specific gravity of diatomaceous earth is some ten times the apparent specific gravity of *ca.* 0·22, which in its turn is about half that of Florida earth (*ca.* 0·43).

The melting-point percentage filler curves (Fig. 4) present several interesting features. Here it will be seen that Redhill fuller's earth, which has won a world-wide reputation as a decolorizer of animal and vegetable oils, is comparatively "inefficient" as a filler. It is significant, too, that unactivated bauxite is only a little inferior in its power to alter the physical properties of bitumen. When activated, *i.e.*, when water of hydration is lost on ignition, the surface area of bauxite per unit weight is greatly augmented, and this factor may really explain its efficiency as a filler. That kieselguhr should also have such a great effect is strong evidence in

support of the theory that changes in physical properties of bitumen on the addition of certain fillers are due largely to the surface area of the fillers themselves, and are due only secondarily to the adsorbent properties of those fillers. Whether or not bodies with a porous structure will adsorb is dependent on the size of the pores, and also on the constitution of the earth themselves.

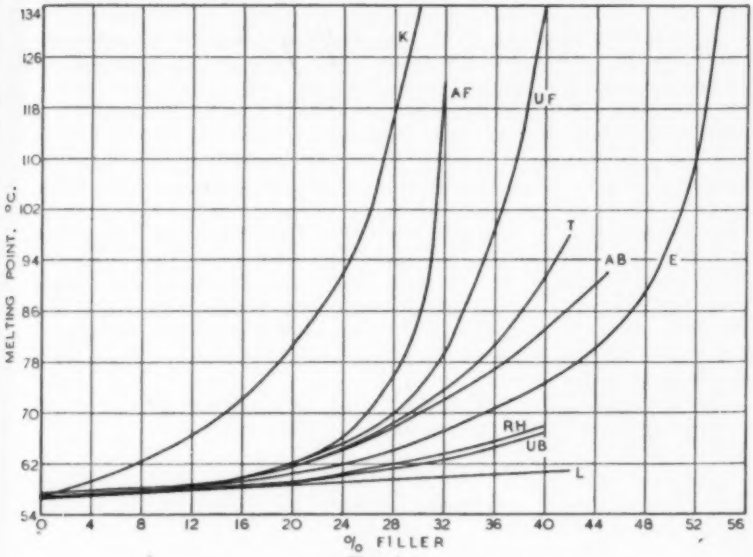

FIG. 4.

For reasons that will be explained later in this paper, the author considers that the power to adsorb *irreversibly* is a surer guide than simple decolorizing tests to a comparison between the properties of fillers. The method, too, of arriving at figures for irreversible adsorption will be described in detail later. For representative figures some 32 per cent. A.C.s were selected, the fillers being the most widely varying in properties. The bitumen was extracted with carbon disulphide, and the weight of the asphalt then adsorbed irreversibly by the filler was estimated.

TABLE I.

Earth.	% by weight of bitumen irreversibly adsorbed by the filler in 32% A.C.	
	After standing for 3 months.	After standing for 12 hours.
U.F.	8·9	9·1
A.B.	6·4	6·2
T.	10·0	8·2

Table I shows that if a cement is kept for some length of time, it is possible for a slow reaction to take place (a point emphasized in the case of Terrana earth). It was noted by Evans [2] that after a few months asphaltic cements develop tensile strength two or three times those they have after mixing. In the light of the experiments just described the amount of adsorption in any case does not increase greatly on standing, so that such increases in tensile strength must be attributed to causes other than a slow adsorbent action.

What is more significant is the fact that the best adsorbent is not necessarily the filler of highest "efficiency." An example of a filler with very feeble decolorizing properties, yet having an "efficiency" between those of epuré filler and of Portland cement, has been cited by Neumann [3] in the case of blast-furnace slag. Here it seems probable that there are present few pores small enough to bring about any appreciable adsorption from solution, yet the presence of larger pores greatly increases the natural surface area of the particles. Kieselguhr demonstrates this phenomenon to a marked degree. The practical use of such fillers, however, presents grave doubts. Several times, *e.g.* in mixing and in melting-point determinations, it was observed that kiesulguhr has a strong tendency to come away from the bitumen. On the basis of these observations a drastic test was devised. About 10 gms. of each A.C. were boiled with 5 gms. of sand and 100 ml. of distilled water for 15 minutes and the resultant effects of this treatment were noted.

The inadvisability of considering kieselguhr as a filler suitable for utilization in cements is clearly demonstrated in Table II.

TABLE II.

Results of Boiling Test.

Earth, per cent.*	Observation.
32 per cent. Kieselguhr	Mostly disintegrated.
32 per cent. Terrana	Melted into small lumps.
32 per cent. Activated Florida	Melted.
30 per cent. Unactivated Florida	Melted.
32 per cent. Activated Bauxite.	Melted into lumps.
32 per cent. Unactivated Bauxite.	Melted and partially disintegrated.
32 per cent. Fuller's Earth XL	Melted into small lumps.

* Percentage of earth in the asphaltic cement.

TEMPERATURE OF ACTIVATION AND THE USE OF EARTHS AS FILLERS.

Of the earths selected, two are capable of being activated by heat; these are the bauxite and the Florida earth. The difference between cements made with activated and unactivated bauxite is as marked as that between the properties of kerosines treated with activated and with unactivated earth. The temperature of activation for this earth was in all cases 400° C.[7]

Florida earth after partial dehydration at 200° C. is only a little more effective after a heat treatment. The earth was activated in an electrically heated muffle furnace at various temperatures for 2 hours. After being cooled in a desiccator, it was incorporated into the bitumen.

An examination of the curves in Fig. 4 indicates that in the case of a cement containing a reasonably high percentage of active filler, the addition of a little more earth results in a notable increase in the melting point. Accordingly, for the following tests, 33 per cent. cements (*i.e.* cements containing 33 per cent. of earth and 67 per cent. of bitumen) were made up.

It is clearly demonstrated (Fig. 5) in the case of Florida earth that a temperature of maximum activation is reached, and that this temperature lies between 500° and 600° C. It is notable that the temperature necessary for maximum possible decolorizing effects lies between within the same limits (500° and 700° C.).

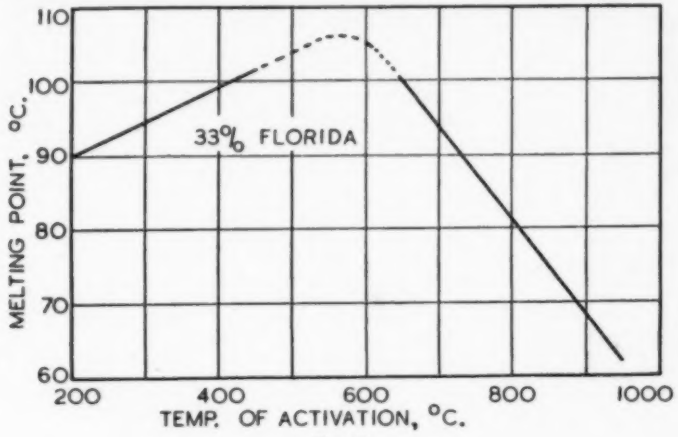

FIG. 5.

THE EARTHS AS DECOLORIZERS.

Having determined the relative values of the earths as fillers, it becomes a matter of interest to compare their power to decolorize petroleum products which are in solution. The contact method of decolorizing as opposed to percolation was used for comparing the earths, owing to the simplicity of working conditions and because consistent results can be obtained more easily.

The exact procedure adopted was as follows :

100 ml. of the solution to be tested were pipetted into an 8-oz. bottle, 10 gms. of the earth in question added, the bottle corked (with a cork protected by tin foil) and then shaken for 5 minutes in a mechanical shaker. The bottle was taken out at the end of this time, the contents were allowed to stand for another 5 minutes, and then all the liquid was decanted through a fine filter-paper. Precautions were always taken against evaporation (by the provision of cover glasses, etc.). As soon as more than 10 ml. had filtered through, the colour of the filtrate was matched against that of the original solution. Although adsorption is usually recognized as complete only after about 20 minutes,[13, 14] it was felt that the shorter period of contact was sufficient for comparing the decolorizing efficiencies of the earths.

The method of measuring the colour changes was based upon the results of the work of Parsons and Wilson.[16] Two exactly similar colour tubes (½ inch diameter) were used, and the darker of the solutions was diluted until the colours matched when lighted in the rear by an ordinary 100-watt lamp. Two solutions were experimented with, namely :—

(1) a 10 per cent. solution of a dark steam cylinder oil in benzene;
(2) a 0·5 per cent. solution of bitumen in carbon disulphide.

Although the defects of comparing such results are many,[11] it appears that the order of decolorizing efficiency is not very different in the two cases (Table III). Trouble was taken to make up solutions of roughly similar asphaltene content, so that any differences between the actions are due undoubtedly to the constitutions of the oils and bitumens themselves. There has been much work done on the subject of adsorption of the same solute from different solvents,[19, 20] but it appears, from experiments carried out by the author, that on a 2 per cent. bitumen solution the amount of colour removed is practically the same whether benzene or carbon disulphide is used.

TABLE III.

Earth.	Percentage Colour Removed.	
	10% Benzene Solution of a Cylinder Oil.	0·5% Solution of "E" Grade Bitumen in CS_2.
Activated Florida *	69	96
Unactivated Florida	54	92
Terrana	47	88
Fuller's Earth XL	31	57
Activated Bauxite †	31	30
Kieselguhr	23	37
Unactivated Bauxite	13	5
Limestone	9	5
Epuré Filler	—	38

* Activated at 600° C. for two hours.
† Activated at 400° C. for two hours.

In connection with the experiments recorded in Table III, it is noteworthy that Neumann and co-workers have measured the adsorbent powers of some earths by a colorimetric method; but unfortunately in all cases the earths selected had relatively feeble effects. In any case, it will be shown that decolorizing properties are not necessarily related to adsorbent properties. Figures have also been given for the decolorizing properties of epuré filler; but all such results must be regarded with suspicion owing to the methods that are necessary to obtain the filler free from organic matter. The best method for obtaining the filler (other than by burning off the bitumen) is by extraction with a mixture of alcohol and benzene.[17, 18] Even so, a used earth after such an extraction in a Soxhlet apparatus, when moistened with a little solvent, is much darker in colour than is the unused earth likewise wetted. It is worth remarking that when the extracted earth is dry, it becomes far lighter in colour and is little different in appearance from the original powder. In the case of epuré

filler, the black or dark grey colour produced on wetting is very pronounced, and this phenomenon may be taken as a strong indication of the presence of small traces of irreversibly adsorbed bitumen.

Limestone as an Adsorbent.

Limestone is only a feeble decolorizer for dilute solutions of bitumen in carbon disulphide. Its action with increased concentration of solid, however, is enhanced in the way to be expected from the Freundlich Adsorption Isotherm.

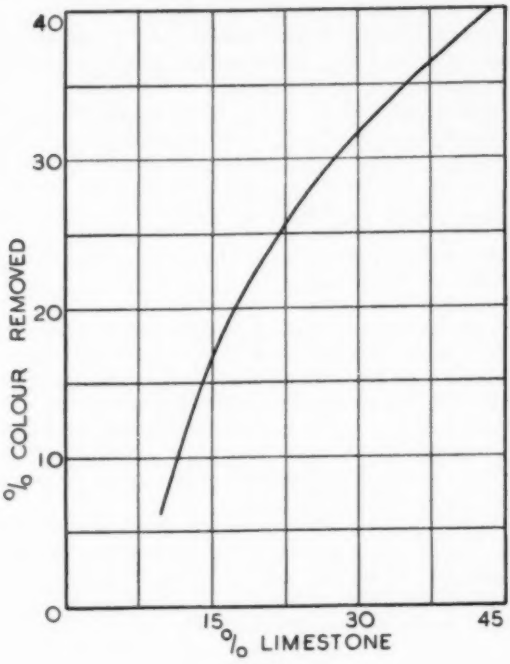

Fig. 6.

It is illuminating to observe from Fig. 6, where a 0·5 per cent solution of bitumen is under consideration, that 10 gms. of activated bauxite are equivalent to only 28 gms. of 120-mesh limestone in decolorizing action on the bitumen solution, and that 10 gms. of kieselguhr are equivalent in action to only 37 gms. of limestone. It seems certain that limestone in sufficient quantity will decolorize asphaltic crude oils, provided that the proportion of limestone is large compared with the crude, and *that the limestone is dry*. The second condition is probably rarely met with in nature, and may account for the fact that in many known cases of migration through limestone the properties of crude oils have not been altered materially.

Irreversible Adsorption.

Until now the adsorptive property of an earth has been measured by its decolorizing ability. The experiments of Gurvitsch [12] have shown that from a solution of resins in benzine the amount of material retained by Floridin when extracted exhaustively with a large excess of the same solvent is not much less than that amount first adsorbed during the decolorization process. In the case of adsorbents, then, decolorization is marked by the fact that, for the most part, the solids taken out are adsorbed irreversibly. In a true estimation of the character of decolorizers, irreversible adsorption plays a fundamental part.

Experiments were carried out to determine the percentage of irreversible adsorption associated with the decolorization of 0·5 per cent. solutions of "E" grade bitumen in carbon disulphide. The apparatus used in extracting the earths employed in the decolorizing experiments was a modification of that proposed by Wilson [23] for the extraction of bitumen from mastic asphalt. An 18·5 cm. filter paper was used in the apparatus, and folded in the special manner suggested. Despite these precautions, however, there was occasionally definite proof that solid mineral matter had crept over the edge of the paper. There were certain contributory reasons for this, *e.g.* the glass plate was not glued to the funnel, although the glass edges of the latter were ground.

The earth-solution mixtures were poured in immediately after the 10-minute period of shaking and settling, and the solids were not allowed to dry on the filter paper, as active earths might possibly polymerize resins, etc., in the presence of air. Water-white carbon disulphide was allowed to percolate through the earths until the filtrates were finally colourless or a very pale straw colour—an operation that usually had finished within a few hours. The used adsorbent, when completely extracted of its reversibly adsorbed bitumen at room temperature, was allowed to dry in the open and then in the steam oven for 1 hour.

About 5 to 10 gms. of the extracted earth were emptied into a porcelain crucible, and an approximately equal weight of the same earth *un*used was added to a similar crucible. After 2 hours drying at 110° C. the earths invariably approximated to a constant weight when cool. Actually these adsorbents were weighed only after drying from 12 to 24 hours. The crucibles and their contents—usually four in a batch, consisting of two samples of each of the used and unused earths—were placed in an electrically heated muffle furnace, and their temperature was brought up to 900° C. during a period of about 2 hours. They were maintained at this temperature for a further period of 1 hour and then allowed to cool, afterwards being weighed. From the differences in weights the percentage of irreversible adsorption can be calculated. Figures were checked by evaporation of the exhaustive extracts.

The distinction between an adsorbent and an absorbent is emphasized by a comparison between the actions of bauxite (activated) and of kieselguhr (Table IV).

Practically all studies in the phenomenon of decolorization by adsorption have been characterized by the fact that increasing weights of earth are used on identical volumes of oil. Consequently it has been found that

TABLE IV.

Earth.	% Colour Removed.*	% Irreversible Adsorption.†	Wt. of Bitumen Adsorbed Irreversibly, gms.
A.F. . . .	96	58	0·29
U.F. . . .	92	41	0·20
T. . . .	88	39	0·20
R.H. . . .	57	16	0·08
K. . . .	37	7	0·04
A.B. . . .	30	30	0·15

* Repeatability 4%.
† Repeatability 2%.
Adsorption from a 0·5% solution of "E" grade bitumen in CS_2.

the results obtained thus are not of much value when another oil comes under consideration. There is another way of approaching the problem, and that is by keeping the weight of solid adsorbent constant and increasing the concentration of bitumen in solution.

The curves in Fig. 7 are based on only two definite points, but their

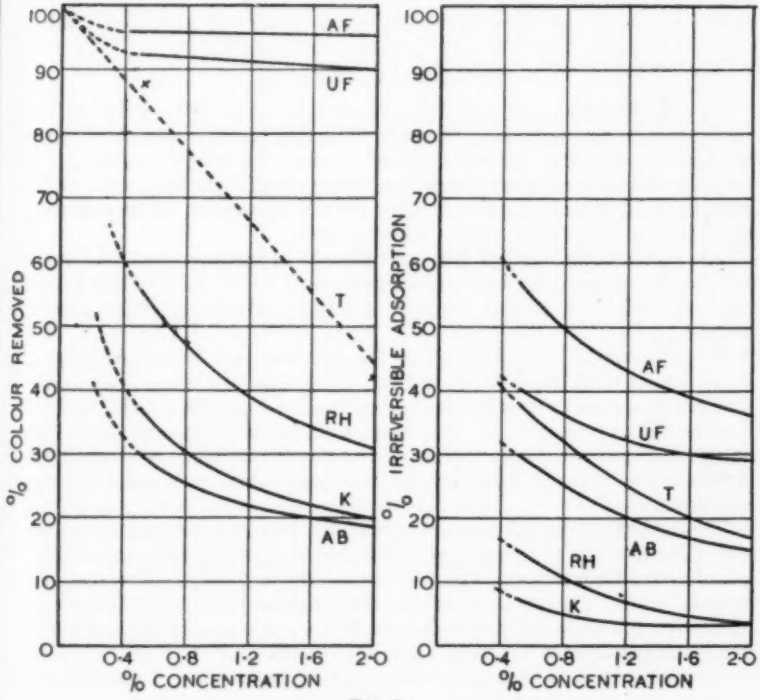

FIG. 7.

tendency is well marked and the concentration of bitumen very low, so that complete justification is felt in their production.

An analysis of the bitumen selected was made with the following results:

Asphaltenes	32 per cent.
Resins	39 ,,
Inert oils	29 ,,

(The arbitrary method selected will be described in detail later.)

Consequently, on the assumption that the earths have no action on the inert oils in the presence of more reactive compounds, only a maximum of 71 per cent. by weight can be adsorbed. Further, most of the colour of the solution will be due to this 71 per cent. The two sets of curves in Fig. 7 show clearly how differently some earths react. Another fact brought to light is that some earths are very much more effective when decolorizing more concentrated (*e.g.* 2 per cent.) solutions. Finally, in the case of bauxite we have the phenomenon of the percentage of irreversible adsorption being higher than the actual weight removed *calculated on the assumption that all colour is due to* 71 *per cent. by weight of the bitumen.* This apparent anomaly may be explained by the conclusion that activated bauxite adsorbs (reversibly and irreversibly) the lighter members of the colloids, and consequently the more lightly coloured bodies. Figures for colour removal are not necessarily representative of adsorbent ability.

Analysis of Extracts.

All the chemical and physical evidence leads to the conclusion that bitumen is an emulsoid sol. Without discussing the dispersion of carbon,[24] the fact remains that the colloidal bodies may, as a whole, be precipitated by the addition of light petroleum ether, liquid pentane, etc. While separation by petroleum ether is incomplete [25] this solvent is very convenient for separating off the so-called asphaltenes.

The non-colloidal bodies that still remain in solution may be divided arbitrarily into petroleum resins and inert oils. The resins may be adsorbed by very active earths, *e.g.* activated Florida earth and the inert oils left behind.

In general, the asphaltenes are the heaviest and most unsaturated; at the same time, most of the colour of bitumen is due to these bodies. The resins appear to occupy a mean position between true colloids and true solutes,[26] and generally contain oxygen or sulphur (dependent on their source). Finally, the inert oils, as their name implies, only react with very active earths under extreme conditions,[28] and have a pale straw colour in solution.

Theoretically it is to be expected, and the previous results seem to bear out, that provided an earth has a suitable coagulating action, a colloidal solution will be precipitated first before a substance that is in true solution is acted upon. Furthermore, in the case of the inert oils it is to be expected that very little reaction will take place in the presence of the much more reactive bodies.[29, 12]

A consideration of these principles prompts the question of what happens during adsorption from a solution of bitumen. The method of analysis

that was used in actual practice was substantially that described by Abraham.[30] Despite the fact that different adsorbents have been advocated for the adsorption of the resins,[14] Florida earth was used after a short drying process at 110° C. It appears that if the active earth is dried too much it *can* possibly react with the inert oils even in the presence of resins. Creeping of the fine powder was carefully guarded against.

Adsorption experiments were performed on 2 per cent. solutions of bitumen in carbon disulphide and the collective exhaustive extracts evaporated down and analysed. It must be remembered that the method of analysis is only arbitrary, so that when the asphaltene percentage is low the figures are more likely to be inaccurate. For asphaltenes 200 ml. of petroleum ether were always used; for resins about 20 gms. of earth were employed.

TABLE V.

Earth.	Analysis of Exhaustive Extracts.				
	Asphaltenes, %.	Resins, %.		Oil, %.	R/O.
		(*a*)	(*b*)		
None . . .	32	39	39	29	1·33
A.F. . . .	13	37	41	50	0·74
U.F. . . .	19	40	38	41	1·0
T. . . .	24	38	41	38	1·0
A.B. . . .	30	38	37	32	1·16
K. . . .	29	39	41	32	1·22
R.H. . . .	32	39	39	29	1·33
	Analysis of Direct Filtrate.				
None . . .	32	39		29	1·33
A.F. . . .	7	54		39	1·40
A.B. . . .	34	37		29	1·32
T. . . .	25	42		33	1·30
K. . . .	33	39		28	1·34

Experiments conducted on a 2% solution of bitumen in CS_2, using 10% of earth. (*a*) Actual. (*b*) Deduced.

$$R/O = \frac{\%\ \text{Resins}}{\%\ \text{Oil}}.$$

In Table V, for the percentage of resins, two sets of figures have been given. Knowing the original composition of the bitumen and the percentage of asphaltenes that have been adsorbed, it is possible, on the assumption that the oils are inert, to calculate the percentage of resins left. It will be seen that the figures (*a*) and (*b*) agree fairly closely. Although the resin percentage appears to remain almost constant it is not possible to state definitely whether or not this is a coincidence at these concentrations.

The second part of Table V shows the results of analyses of direct filtrates, *i.e.* the filtrates obtained from simple decolorization experiments. The figures R/O show clearly how the reactions have progressed on the addition of excess solvent to remove the loosely held colouring matters. A close consideration of the results leads to the interesting conclusions that asphaltenes are adsorbed irreversibly and may only be washed out to a very slight extent.[31] The adsorption of resins is partly reversible, but that of inert oils is almost entirely reversible.

Another set of figures can be calculated from those contained in Table V.

TABLE VI.

Earth.	% I.A.	% A.A.	% R.A.	A/R.
A.F.	36	73	36	2
U.F.	31	60	30	2
T.	17	37	13	3
A.B.	15	19	19	1
K.	5	14	3	4
R.H.	4	4	3	1

I.A. = Irreversible adsorption.
% A.A. = % of asphaltenes that have been irreversibly adsorbed from the solution of bitumen, compared with the original concentration.
% R.A. = % of resins " " " " " "
$A/R = \frac{\%A.A.}{\%R.A.}$, which gives an idea of the relative activity of an earth to adsorb resins in the presence of asphaltenes.

The figures in Table VI have again been obtained for 2 per cent. solutions of bitumen in carbon disulphide. Knowing the original composition of the bitumen and its composition when an earth has adsorbed a certain proportion and has been washed out exhaustively, the individual percentages of asphaltenes and resins that have been irreversibly adsorbed in the presence of each other may be worked out. The figures are most useful for a comparison of the type of action and the rough ratio A/R gives a good idea into what category an adsorbent may be assigned. Terrana, for instance, exhibits a preferential adsorption of asphaltenes. In the case of bauxite and fuller's earth, there is an equal tendency to adsorb resins and asphaltenes in the presence of each other, despite the customary superior attraction for the more unsaturated bodies. The figures for kieselguhr are low, but indicate a definite preference for colloidal bodies. Florida earth is the most efficient adsorbent, and besides taking out asphaltenes, still reacts with a large proportion of the resins. This table appears to be a sound guide for the used of mixed adsorbents. By the utilization of certain combinations of earths it would seem possible to decolorize asphaltic oils to predetermined limits, removing asphaltenes and at the same time controlling the percentage of resins.

ADSORPTION OF ASPHALTENES.

The results obtained in the complicated case of adsorption from a solution of asphaltenes, resins, and inert oils together, prompts the question of what happens with resins and asphaltenes separately in solution. Petroleum ether provides a convenient means of separating bitumen into the two main classes, colloidal and non-colloidal bodies.[32] The petroleum ether–bitumen ratio was observed strictly for comparative results, so that 20 gms. of the asphalt were treated with 2 litres of 40–60 petroleum ether and left for 24 hours in the dark. Ultimately after washing out resins and oils, two solutions of asphaltenes were made up containing:

(*a*) 0·64 per cent. asphaltenes in carbon disulphide;
(*b*) 2 per cent. asphaltenes in carbon disulphide.

The first solution contains a percentage of asphaltenes (0·64 per cent.) equal to that found in a 2 per cent. solution of bitumen. As before, decolorization tests and estimations of the percentage of irreversible adsorption taking place with the addition of 10 per cent. of earth were performed in the cases of the earths of most distinct type.

A comparison between the two sets of curves depicted in Fig. 8 allows several conclusions to be reached. In the first place, it is roughly true that in some cases the adsorptive ability (which is probably wholly irreversible

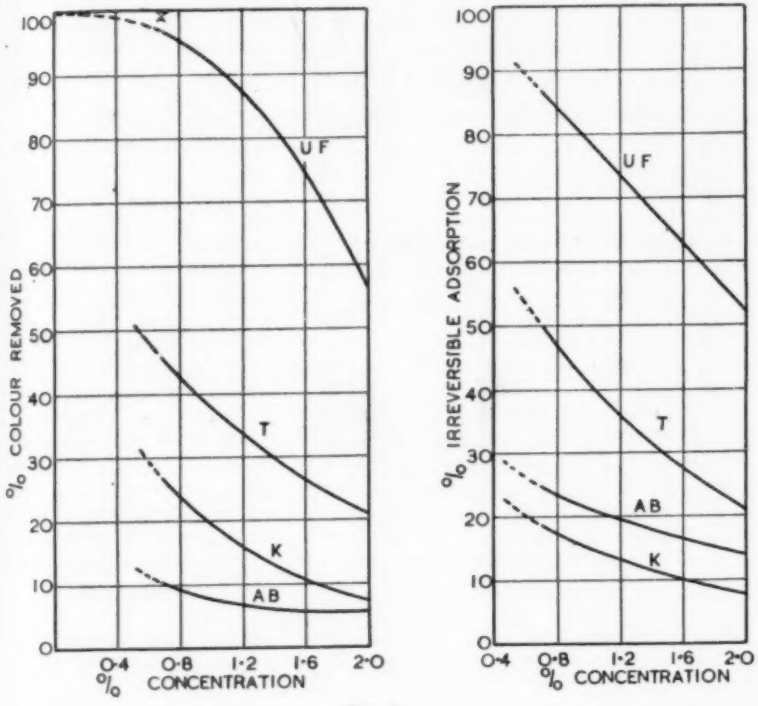

FIG. 8.

in these cases) is equal to the decolorizing ability, at least at these low concentrations. Cases in point are those of Florida earth and Terrana earth. On the other hand, kieselguhr and activated bauxite present two very different cases. The general character of bauxite is a strong indication that practically all adsorption by this earth from colloidal solutions is irreversible. Accordingly, the fact that the figures for irreversible adsorption are two to three times those of colour removal, suggests that another explanation, based on the difference in molecular weights of the asphaltic bodies present, is necessary. Such an explanation suggests that while Florida, Terrana, and kieselguhr adsorb equally well over the whole range, activated bauxite has a preferential tendency to adsorb the low-molecular-weight compounds.

The figures obtained for colour removal at the smaller concentration suggest definitely that while Florida earth may exhibit a tendency to take out the very heavy bodies first, the reverse is true for activated bauxite.

Independent figures for English fuller's earth show that this is a little more efficient than bauxite, and is very similar in its action in connection with asphaltenes. Epuré filler was also experimented with, and was shown to have good decolorizing properties, ranking it just below Terrana.

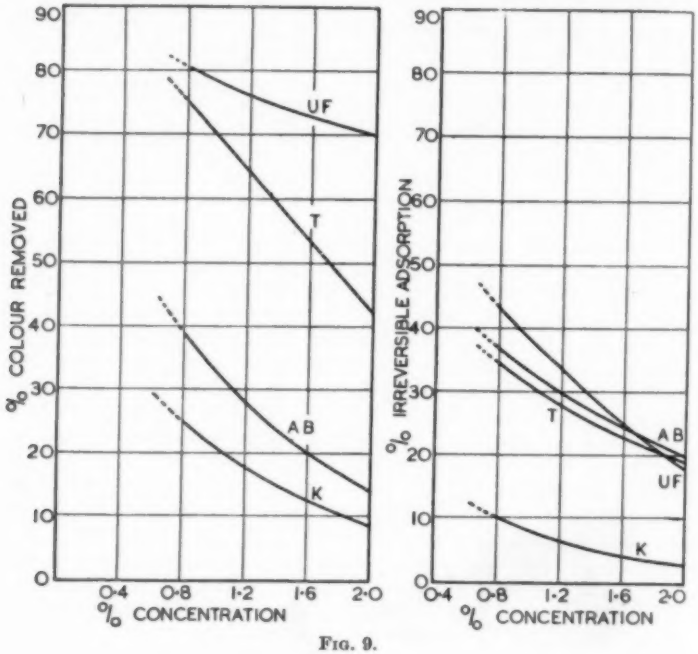

FIG. 9.

ADSORPTION OF RESINS AND INERT OILS.

Analysis shows that 20 gms. of bitumen contain 13·6 gms. of resins and inert oils, soluble in petroleum ether. In practice two solutions were made up containing:

(*a*) 1·36 per cent. of resins and inert oils in carbon disulphide, or 0·78 per cent. of resins in carbon disulphide;

(*b*) 3·49 per cent. of resins and inert oils in carbon disulphide, or 2 per cent. of resins in carbon disulphide.

The earths were again tested by contacting, followed by filtration, in exactly the same way as the solutions of bitumen and of asphaltenes had been treated. As before, after the decolorization experiments, the earths were exhaustively extracted and the amount in weight of irreversible adsorption was determined (Fig. 9).

In the first place, most of the colour of the resin and oil solutions is due to the 57 per cent. of resins. The lines have been plotted on the assumption that the adsorption of inert oils is negligible when resins are present. The resins remaining after contact filtration have been estimated by adsorption in the Soxhlet apparatus with dried Florida earth. The figures have been checked also by evaporation of the exhaustive extracts. It is emphasized once more *that the figures for colour removal are found from the direct filtrates*; those for irreversible adsorption from the exhaustive extracts.

In some cases it was noticed that the exhaustive extracts, when concentrated to their residue, exhibited a cloudy appearance, but tests showed that the weight of cloudy matter insoluble in petroleum ether was exceedingly small.

The first significant point about the results is that the weights of irreversibly adsorbed material is in all cases comparatively small. This is due almost certainly to the fact that only a certain amount of adsorption in these cases is irreversible.[31] According to Nellensteyn,[24] separation of bitumen into colloids and non-colloids by petroleum ether is incomplete and these latter bodies may further be separated by solution in acetone. Another remarkable fact is the failure of Terrana earth at higher concentrations—a point that was noticed in the case of adsorption from solutions of bitumen itself. The phenomenon may be explained on the assumption that the acid activated clay has the individual tendency to take out compounds of a lower molecular weight than has Florida earth. At lower concentrations, when this specific range is much smaller in quantity, it takes out higher molecular weight bodies as well, and thus its decolorizing efficiency is increased. Alternatively, it may absorb equally well over the whole range. In the case of activated bauxite we again have a remarkable demonstration of its ability to adsorb resins, but preferably those of lower molecular weight. Kieselguhr does not hold firmly resins which it adsorbs, and also probably reacts in the first place with that small proportion of colloids adventitiously present.

Polymerization of Resins.

Bleaching experiments performed on light distillates by various authors[34, 7] point towards the fact that decolorization is usually accompanied by polymerization or chemical reaction. In certain cases there may be no polymerization.[34] The method developed for ridding epuré filler of its last traces of irreversibly adsorbed material by the use of the mixed solvent, alcohol and benzene, suggests a convenient means of determining whether or not polymerization takes place during the adsorption of resins derived from a residual bitumen.

The experiments already performed with the earths and a 2 per cent. solution of resins in carbon disulphide were repeated. The powders thus obtained after complete extraction with the solvent were put into the thimble in a Soxhlet apparatus, and then extracted with a 50–50 benzene–alcohol mixture. By this means a further weight of adsorbed colouring matter was extracted. The moist residual earths were all but a shade darker than the original specimens, and when dry little difference in colour could be detected. Hence, although there was some, there can have been little

organic matter left behind by the last extraction. It is noteworthy that during an attempt to extract the earths with alcohol alone, although the process was slow, it appeared in the case of activated bauxite that more colouring matter could be extracted than in the case of any other earth. The results are summarized in Table VII.

TABLE VII.

Earth.	% Extracted by CS_2.*	% Extracted by C_2H_5OH and C_6H_6.*
U.F.	82	95
T.	81	94
A.B.	80	96
K.	97	*c.* 99·8

* Referring to the percentage of resins extracted and disregarding the presence of inert oils.

The colouring matter thus extracted was treated with light petroleum ether to separate off asphaltenes, but in all cases this percentage was low. By dissolving all the extracted bodies in 100 ml. of carbon disulphide, the colours of the solutions were compared with the colour of the original solution. In every case there was almost no distinction, so one must conclude that the *so-called chemically active earths do not polymerize the resinous bodies contained in bitumen to any appreciable extent, when used in the conditions under which these experiments were conducted.*

CONCLUSIONS.

(A) *The earths as fillers:* The results obtained with the various fillers lend support to the theory that their "efficiency" is not directly proportional either to their adsorbent or decolorizing properties. On the other hand, the bleaching power of a clay is often a secondary point dependent on the surface area due to particle size, and/or inherent porous structure. Nevertheless, such clays and earths as have been used in the petroleum industry for decolorizing oils are usually fillers as efficient or more so than epuré filler.

It is a notable fact that earths that can or must be heat-activated before use as decolorizers, when employed as fillers show a similar improvement upon their "efficiency." It seems probable that this phenomenon is due largely to the additional surface area thus made available by loss of water and subsequent increase in the porosity of the individual particles. As far as the active earths are concerned, then, it is of little use evaluating the particle size distribution owing to:

(*a*) the increase of surface area due to the presence of pores;
(*b*) the adsorption that takes place within some of these pores.

An extreme case of an earth having a remarkable porous structure, few really small particles and little adsorbent ability is provided in the case of kieselguhr. This diatomaceous earth has a greater effect on the physical properties of a bitumen than any other earth that has so far been investigated.

The property of adsorption may, however, still be of importance in the

consideration of an active earth potentially suitable as a filler. Active earths probably bind with the asphaltenes contained in bitumen on account of the colloidal nature of these bodies, and consequently the higher the adsorbent properties, the firmer becomes the binding power. In some cases where binding power is poor it is relatively easy to break up the cement.

Epuré has enjoyed a reputation that is bettered by no other cement, but the production of an artificial competitive material would appear to depend upon the following three main points:

(1) the selection of a suitable bitumen;
(2) the surface area of the filler due to—
  (*a*) fineness of division;
  (*b*) porous structure of the individual particles;
(3) the adsorbent properties of the filler in relation to the asphaltenes.

With epuré filler it is to be remembered that it is extremely finely divided. In theory, at least, then, provided conditions (1) and (2) (*a*) are fulfilled satisfactorily, a cement can be compounded the properties of which will be superior even to epuré. One result of the researches described in this paper has been to demonstrate that it is conceivably an economic procedure to utilize spent decolorizing earths as fillers for asphaltic cements.

(B) *The earths as decolorizers:* Before the true character of the earths as adsorbents can be estimated, some mitigating factors must be emphasized. In the first place, there is a certain amount of wax present, but this is spread throughout the classes when a separation is made.[28] Secondly, but a far more important factor, is the presence of some 5 per cent. of sulphur compounds. Some earths (*e.g.* activated bauxite) have a much more marked tendency to adsorb sulphur compounds before bodies of another nature. The case, too, may be quite different from that when kerosines are under consideration.[7] Most of the experiments on which these observations are based were performed on the colouring matters found in the residual product of a vacuum distillation of a Mexican crude oil to about 320° C. Consequently, the deductions are limited to consideration of the "heavy" petroleum bodies, *e.g.* cylinder oils, waxes, etc.

It has been shown that the decolorizing power of a clay may bear little relationship to the actual weight of material adsorbed, and still less to the percentage of colouring matter that is irreversibly adsorbed. Further, the ease with which asphaltenes (and probably, too, bodies coagulated by the addition of acid) are precipitated by earths is not related necessarily to the activity such earths display when used for decolorizing solutions of resins. The discussion can be illustrated best, perhaps, by considering each earth separately.

Florida earth exhibits both marked precipitating and decolorizing properties. It is capable of removing the asphaltenes from petroleum products, ranging from the lighter bodies to those of extreme molecular weight; nevertheless it appears to display a preference to adsorb the very heavy end of the range of bodies which may be treated. With a solution of heavy resins its property of reacting preferentially with the darker and heavier members is very marked, and its irreversibly adsorbent properties may be only moderate.

Terrana earth is similar in action to Florida, but both in solutions of asphal-

tenes and of resins the average molecular weight of the bodies removed is probably somewhat lower than that adsorbed by the latter earth. In practice, however, Terrana is usually employed after a preliminary acid treatment of the oil in question.[33] It is claimed that this earth has a specific adsorbent action on the sulpho-bodies formed, as well as on the irreversibly coagulated asphaltic matter [21]; it has been stated also that the removal of sulpho-bodies prevents colour reversion.[22] This information has been included because it is felt that the tremendous difference in action brought about by varying the conditions of treatment is not generally realized. With an increase in concentration of the colouring matter Terrana displays an individual characteristic of failing to decolorize so well as Florida. This tendency is especially marked when dealing with resins where reversible adsorption may be taking place.

In the presence of asphaltenes, activated bauxite partly retains its activity to react with resinous bodies. In the latter case this earth displays a marked inclination to remove the more lightly coloured bodies in preference to the darker bodies. Consequently, this earth is unsatisfactory as a decolorizer of heavy oils, whether asphaltic or not. Only if the resins are of low molecular weight (as in light distillate oils) can it be expected to give a reasonable decolorization per unit weight.

Of the Redhill fuller's earth little can be said, save that it is closest to activated bauxite in its action. Nevertheless, it must be considered as belonging to a different type.

The consideration of such an earth as kieselguhr opens up the fascinating possibility of utilizing clays with absorptive properties. In commercial use the theoretically ideal earth should have the following properties:

(*a*) high decolorizing ability;
(*b*) low irreversible adsorption.

In no case investigated, however, has a decolorizer both properties developed to a high degree.

An interesting fact brought to light in these researches is that the resins during adsorption are not polymerized and do not change much in properties on account of the earth treatment. Under the conditions employed, only minute quantities of asphaltic material may be formed even when using very active earths. For light petroleum products chemical action is often pronounced; for the heavy products it is difficult to detect.

(C) *Geological significance:* Limestone has been shown to possess definite decolorizing properties when used in large enough quantities. To show that this activity was not in any way limited to artificial solutions of bitumen in carbon disulphide, the results were confirmed by the use of asphaltic crudes.

In actual practice, however, it is probable that results obtained with wet limestone will prove of more value and wider application. Although it has not been possible to investigate this point further, it has been found by the author that limestone will not decolorize emulsions of equal quantities of crude oil and water. The course of the reaction, however, cannot be predicted definitely, when only, say, 2 per cent. or less of water is present.

One concludes that in the migration of oil through a fault in a limestone bed under conditions of dryness there will be an alteration in the properties

of any asphaltic crude. When water is present, and with the existing knowledge available, little can be predicted. Although it has been shown that crudes do alter in chemical characteristics when apparently from the same source, it is shown now that it is not at all necessary that the asphaltic oil should pass through a bed of active clay to bring about the transformation. Under conditions of percolation whereby any earth will exert a maximum effect, dry limestone is capable of showing a very pronounced decolorizing action.

ACKNOWLEDGMENTS.

Various companies have kindly contributed materials used in this research, and among them are: Messrs. Rudolf Hermann and Co., who supplied bauxite, Terrana earth and Florida earth. The Fuller's Earth Union of Redhill (Surrey), who donated supplies of grades of fuller's earth; Messrs. Shell Mex and B.P. Ltd., who contributed the bitumen used, and the Limmer and Trinidad Lake Asphalt Company, who supplied the limestone.

The author begs to acknowledge gratefully the kindly interest and advice of Professor V. C. Illing, and also the unfailing help and direction given by Mr. A. Wolf at difficult periods.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Forty-fifth General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on the 27th January, 1936, Mr. G. H. Scott, B.Sc., acting as Chairman.

The Chairman apologized for the absence of Commander H. V. Lavington, R.N., Branch Chairman, through indisposition.

He then referred to the great loss occasioned by the death of His Late Majesty, King George the Fifth, and suggested that the meeting should record its feelings of loyalty and esteem by standing a few moments in silence. This tribute was duly accorded.

The Chairman then called on Mr. H. A. Harris to read the following paper :—

COST OF DRILLING.

By H. A. HARRIS.

INTRODUCTION.

In the technical literature there are few, if any, text-books on costing for a producing oil company, although much has been written on the refining end of the industry.

Therefore it may be of interest to describe briefly a method of costing the drilling of wells which has been employed by a producing company in Trinidad.

Whilst, from the nature of the subject, it is necessary to make a somewhat bald tabulation of the items charged to the cost of drilling, it is hoped that the discussion will serve to amplify and elucidate any points that have not been adequately explained.

GENERAL PRINCIPLES.

The main functions of a producing company are first to drill to the oil-sand and then to produce the oil.

Thus, in framing the Costing System, the fundamental principle has been to make a broad division under these two main headings, viz. :—

Drilling—Wells Cost,
Producing—Production Expenses,

and to allocate all normal charges against revenue to one or the other of these headings.

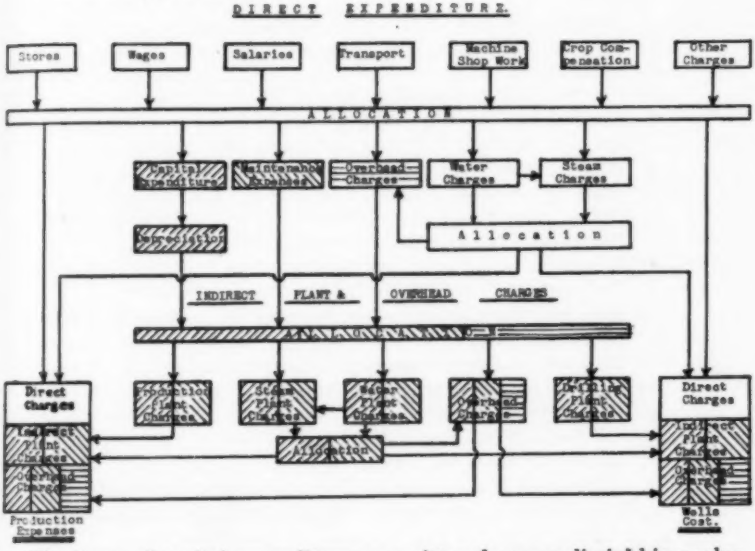
That is to say, the final Costs are " All-in " costs.

The Costing System.

Before proceeding to enumerate in detail the items included in wells cost, it is necessary to give some explanations regarding the Costing System in general.

All direct expenditure—labour, supervision, materials and other expenses —is charged under five main headings :—

1. Capital Expenditure :
   Machinery, pipe-lines, tanks, buildings, roads, dams, etc.
2. Maintenance Expenses :
   Repairs, renovations and replacements of parts, etc., of the above.
3. Wells Cost.
4. Production Expenses.
5. Overhead Charges.



The items of capital expenditure are written down on diminishing value at rates adequate to cover useful life.

The amount of depreciation in this way is greater initially than by writing down on first cost over the period of life, but this is offset by the increasing cost of maintenance with age.

All new units of plant, whether additional or replacement, are charged to capital account.

To the direct costs of wells cost and production expenses are added "Indirect Charges," such consisting of depreciation and maintenance directly applicable to those two operations and being :—

i. Water Supply Charges.
ii. Steam Supply Charges.
iii. Plant Charges.

The totals at wells cost and production expenses at this stage are known as "Total Working Costs."

The remainder of the depreciation and maintenance expenses, which have not been allocated to one or other of the main headings, are deemed to be "Indirect Overhead Charges."

These, with direct overhead charges, are apportioned to wells cost and production expenses, pro rata to their total working costs, the resultant totals being "All-in" costs.

Wells Cost.

Hereunder are listed in detail the items included in all-in wells cost, some of which, of necessity, require explanations which are given in the notes hereto :—

1. *Direct Cost* :—
   - *a*. Clearing site and crop compensation (if any).
   - *b*. Earthworks—levee, pits, tank sites, etc.
   - *c*. Entry road.
   - *d*. Derrick, pipe racks, sheds for engine, pumps, etc.
   - *e*. Rigging up and down of machinery.
   - *f*. Drillers—including drillers dead time (leave pay).
   - *g*. Drilling crews and supplemental labour.
   - *h*. Supervision—tool pushers and drilling superintendent.
   - *i*. Casing, tubing, casing head and well pump when installed.
   - *j*. Transport—running expenses and loading labour.
   - *k*. Electrical coring and deviation surveys.
   - *l*. Tool dressing and other machine shop work.
   - *m*. Mud treatment at well—barytes, aquagel, quebracho, silicate, caustic soda.
   - *n*. Mud and barytes recovery plant expenses.
   - *o*. Part field water supply (see Note 1a).
   - *p*. Part field steam supply (see Note 2a).
   - *q*. Oil used for washing wells.
   - *r*. Rental for tools borrowed.
   - *s*. Allowances of soap and distillate to drilling staff and crews.
   - *t*. Miscellaneous—any other expenses directly chargeable.

2. *Indirect Charges* :—

   Depreciation and maintenance of plant, etc., relative to :—
   - *a*. Part field water supply (see Note 1b).
   - *b*. Part field steam supply (see Note 2b).
   - *c*. Drilling plant (see Note 3).

3. *Overhead Charges* :—

   (i) *Direct* :—

   The proportionate part of the total expenditure on the following :—
   - *a*. Audit fees.
   - *b*. Building allowances.
   - *c*. Sanitation and cleaning and brushing.
   - *d*. Part field water supply (see Note 1a).

e. Domestic water supply (see Note 4a).
f. Bonus to staff.
g. Motor-car expenses.
h. Compensation for pollution.
i. Donations and entertainment of staff.
j. Geological, surveying, drawing office and laboratory expenses.
k. Insurances.
l. Legal expenses.
m. Licences, rents, taxes and wayleaves.
n. Medical expenses.
o. Management and entertainment allowances.
p. Office expenses including bank charges, cables, postages, stationery and printing, periodicals, telephone charges, etc.
q. Field police.
r. Petroleum office expenses (Ordinance No. 8 of 1929).
s. Stores management.
t. Service leave and sick pay—workmen.
u. Travelling expenses.
v. Miscellaneous—any other overhead expense.

(ii) *Indirect*:—

The proportionate part of the total depreciation and maintenance expenses of the following:—

a. Buildings and fittings.
b. Furniture and equipment.
c. Electric lighting and telephone installations.
d. Domestic water supply (see Note 4b).
e. Roads—main and branch.
f. Recreation ground and tennis courts.
g. Motor-cars, lorries, tractors and trailers.
h. Plant and tools of shops—machine, blacksmiths', welders', carpenters'.
i. Pipe and timber racks.
j. Fire extinguishers.
k. Part field water supply.

Conclusions.

It is considered that until proper charges have been made for the use of plant for drilling and for all ancillary services true drilling cost, for comparison purposes, is not obtained.

The costing system outlined adequately provides for the costing of drilling per foot and of production expenses per barrel during the life of a producing oil-field. In the early days expenses are mainly on drilling—later, the stage is reached when expenses on drilling and on production are equal—finally, when drilling ceases, all expenses are on production.

Appreciation.

The author desires to thank Messrs. Apex (Trinidad) Oilfields, Limited, for granting permission to read this paper.

Notes.

Note 1.—Field Water Supply.

(a) *Direct Cost :—*

Expenses of water pumping stations.

(b) *Indirect Charges :—*

Depreciation and maintenance of :—

Dams, pipe-lines, tanks, pumping stations, etc., used for the field water supply.

The totals of (a) and (b) are allocated, on consumption basis, to :—

Wells cost —water for drilling.
Field steam supply—boiler feed supply.
Overhead charges —camp supply.

Note 2.—Field Steam Supply.

(a) *Direct Cost :—*

Boiler plant expenses.
Part field water supply (see Note 1a).
Oil fuel—at sale value.
Gas fuel—at value of oil saved.
Moving boilers.
Boiler inspector's fees.

(b) *Indirect Charges :—*

Depreciation and maintenance of :—

Boiler plants.
Steam pipe-lines.
Pipe-lines—oil and gas fuel.
Fuel tanks.
Part field water supply (see Note 1b).

The totals of (a) and (b) are allocated, on consumption basis, to :—

Wells cost.
Production expenses.

Note 3.—Indirect Drilling and Other Plant Charges.

(a) *Drilling Plant :—*

Depreciation and maintenance of all drilling plant and accessories including drill pipe, tools, fishing tools, cementing outfit, etc.

(b) *Other Plant :—*

Depreciation and maintenance of mud and barytes recovery plants, and of dams, tanks, pipe-lines, pumps, etc., used for mud supply.

The totals of (a) and (b) are charged to wells cost.

NOTE 4.—DOMESTIC WATER SUPPLY.

(a) *Direct Cost :—*

Cost of purification and pumping station expenses.

(b) *Indirect Charges :—*

Depreciation and Maintenance of :—

Water treating plant and of tanks, pipe-lines and pumping stations used for the domestic supply.

The totals of (a) and (b) are charged to overhead charges.

DISCUSSION.

MR. E. COOPER SCOTT took it that the object in view in costing was control, and therefore the system which permitted control was to be aimed at. Control was difficult without comparative figures, and comparative figures should be as simple as possible, and not involved in any way by extraneous conditions. That was especially the case when there was more than one unit field or a group of fields under one control to be scheduled for. In those cases comparisons might become very odious unless they were as simple as possible and devoid of any of the surrounding circumstances which affected separate fields.

From the drilling superintendent's point of view the speaker did not think the former should be asked to take account of any costs other than those for which he was directly responsible, and in Mr. Harris' system, therefore, the allocation of expenditure might possibly stop at direct costs and maintenance of plant directly applicable to the operation of drilling. Overhead charges as detailed in the paper were uncontrolled by the drilling and production departments, and they were therefore probably arbitrarily apportioned, and he presumed it was left to the accountancy branch to apportion it. The author would correct him if it were not so. In that connection he had often wondered why it was that the accountant's apportionment of such expenditure was always taken as being above suspicion whereas such allocation of expenditure on the part of the field staff was taken as very dubious, and very often to exhibit criminal instincts.

It would be interesting for the author to tell them whether the overhead charges varied much, and if not, whether any set charge per barrel and per foot to cover such charges could not be added to tell a reasonably true story of total " all-in " costs.

He would also like to ask if the author would allocate the costs of marketing, refining, advertising, etc., if the company was involved in such operations. He was sure it would be seen that the system would become very involved in such cases.

The question of depreciation was a very debatable subject, and seemed to be entirely a matter of company policy, so that the figure must necessarily be arbitrary. Some companies carry tools and machinery on capital account, which is written down a fair percentage every year; some form a separate capital account, which hires the machinery at a set rate to provide for rentals, repairs, etc.; others, again, charge all machinery direct to working costs, in which case it never at any time figured as capital, so

that no depreciation was necessary. All those systems had their advantages and disadvantages, but the speaker suggested the central equipment capital account had more to recommend it than the other two, especially for a company operating several fields, as it permitted efficient and up-to-date machinery having a fair chance to show its value over a period longer than one year. It permitted the transfer of suitable machinery from field to field, and thus lessened the total amount of machinery in an organization, also it decreased the bugbear of the capital asset which, like the poor, they had always with them. Many present had had, no doubt, to dig up some unrecognizable chunk of metal and exhibit it so as to satisfy the accounts department that it was something which had been operating for a number of years. He had heard it stated that the objection to that account was that it might be used as a wastepaper basket, and permitted the controlling operator to commit to the dustbin anything which he had bought which was inefficient, and also that machinery was lost sight of. The speaker thought if such account was carefully controlled such things should not happen. Once it was started he did not see why such an account could not be balanced and written off to working costs every financial year, if higher accountancy demanded it. He was willing to stand corrected from the accountant's point of view.

The speaker wondered whether the cost per barrel or cost per foot told all the story, and he asked whether the adoption of costs per hour for drilling and cost per well for production, as being additional figures worthy of comparison, were not necessary. The cost per barrel—"all-in"—was the most important figure from the company's point of view, but for control it was confusing to include in cost per foot any outside expense which the drilling department was not responsible for.

Mr. H. A. Bennett said that the system outlined had, he knew, been largely developed by the author himself, and he had brought to bear upon it all his very great capacity for careful and interested study of the hundred and one problems which arise in the development of such a system; furthermore, he had secured the interested co-operation of the technologists in his company, and in doing this, he thought the author was well on the way towards designing a successful costing system; for no system could be regarded as successful unless the *modus operandi* could be followed, and the figures evolved used, by the practical man.

However, it did not follow that a costing system which suited a comparatively prosperous company was that which would prove most suitable for the oil industry at large. Speaking generally, it was to be expected that the reverse would prove to be the case. In any event, there were several points on which the speaker found himself in disagreement with the paper which the author had read.

The speaker thought that in considering a system of drilling costs, it was first necessary to decide what was the goal at which to aim. Drilling costs were certainly not introduced for the amusement of the accountant. The text-books, so far as the speaker remembered, said that the main purposes of costs were two-fold: first to provide a figure to check whether a given product was being produced at a profitable price; and secondly, to provide detailed statistics for the technologists by use of which they

might put the brake on any increasing expenditure and also find avenues for reducing expenditure. This latter purpose was known as control, of which Mr. Scott had spoken.

In the case of drilling wells they were concerned with arriving at the cost per foot drilled. That figure should be one which would enable the technologists to decide whether a programme of wells, to be drilled to a given depth, was likely to cost more or less than the net value of the estimated production at the well head, the net value in this case being selling price less lifting, collection, delivery and royalty expenses. Looking at the system mentioned by the author, the speaker could not find that the figures obtained at any stage could be used by the technologists in the way he had described. The speaker thought that this was due to two main causes : the first and most important being the misconception on which the costs had been designed. The author had said that the main functions of a producing company were first to drill to the oil-sand and then to produce the oil. That the speaker thought was wrong. He held that the main functions of a producing company were, first, to obtain the land on which to drill, second to explore the land by geological survey, third to exploit the land in the manner outlined by the author, and finally to sell the oil produced. If this were accepted, the distribution of all expenses between drilling and production expenditure could not be justified. Take, for instance, rents. What had rents to do with drilling ? To charge this item to drilling expense was, the speaker thought, putting the cart before the horse, for rents must be paid before drilling could commence. In the same way at least a part of office expense. Geological expense and administration expenses had to do with the tenure of land, with its exploration or with the sale of the product, and had no place in the costs of either the drilling or production operations of the company. For this reason, the speaker would draw up the final cost of the production statement differently from the author; he would show in it as well as production and drilling expenditure, the cost of geological survey, the cost of land tenure—that is, rents and licences and legal expenses—and finally that proportion of office and administration expenditure which was not allocated to production and drilling. This would leave drilling costs charged only with those items which were directly or indirectly attributable to the operation.

His next point was the form of the costs, which he regarded as a matter of the utmost importance, for unless the drilling costs were in a form which could be readily understood and used by the technologists, much of the usefulness of the costing system would be lost.

What did the costs in the form outlined by the author tell you ?

Take, for instance, the sub-heading, direct costs. Part of the transport expenses were included, but not the maintenance and depreciation of the trucks and tractors. Rental was charged for tools borrowed, but not for the company's equipment. Tool-dressing and machine-shop work was charged, but this did not include the maintenance and depreciation of the shops and machinery.

The speaker could see no object in dividing the costs into the headings, direct cost, indirect charges, overhead direct and indirect, which meant nothing except to the men in the office. He thought that the best basis

to work on was to regard the drilling department as one which was obtaining goods, labour or service from practically every other field department, and that the charges for same were all direct. This necessitated a proper job-costing system for machine-shop work which included the overhead expenditure of the shop. The charge for an item made in the machine shop could then be compared with the price of the same item from the store, or both items would be charged in the same way.

Transport costs would be worked out on a ton-mile basis, and could be then compared with contractors' quotations.

Superintendence, which should include salary, living expenses, car expenses, etc., of the men concerned, should be distributed on the basis of direct wages.

Steam expense, water expense, light expense, etc., should be charged on the basis of work done by each station, this information being rendered by the engineer responsible.

The speaker agreed with Mr. Scott's recommendation that depreciation should be charged out on a hire system. He could find very little in favour of the author's suggestion that depreciation and maintenance of machine shops, cars and lorries, etc., should be treated as "Indirect Overhead." It might be argued that these charges continue whether the work is done or not, but this was a very short view to take. The field staff should share in the responsibility for this plant depreciation and maintenance. They created the demand which necessitated its installation, and their costs should, therefore, bear the full burden for the work turned out.

With such a system the accountant could be called upon by the technologists concerned to produce documentary evidence for all the charges against drilling wells. Further, the technologist would be supplied at the end of each month with the total and final cost of each well completed, and the charges entered against the wells in progress.

The speaker recommended the following sub-heads for drilling costs:

(1) Preliminary cost—including the cost of preparing the site, erecting the derrick and rigging up the machinery.
(2) Drilling expense—*i.e.* the cost of making hole.
(3) Casing cost.
(4) Dismantling cost.

These headings, he said, provide very useful data for comparison from month to month, year to year, from well to well and field to field. Facility of comparison in costs helps the technologist very greatly in the control of expenditure, and for this reason the speaker urged that above all things the basis of allocations should be consistent.

There was another matter of principle which cropped up in the system outlined by the author on which the speaker would be interested to hear his and other views: he referred to the practice of charging gas burnt in the boiler stations—and presumably internal-combustion engines. He understood that the chief reason in favour of charging gas was that it provided a comparative running cost for boiler stations, internal-combustion engines, compressors, etc., which could be set against the cost of any similar plant operating elsewhere in the world. This was of undoubted

advantage; but there was another school of thought which pointed out that there was no market for gas in Trinidad, and that if it were not used in the field operations it would be blown off to atmosphere, or at best returned to the strata; and that to give this gas the value of fuel oil was to introduce a profit factor which was contrary to the principles of costing. The matter was of some importance, as quite a considerable sum of money was involved, as would be seen from the following figures: A conservative estimate of the gas consumed in a field where six strings were in operation was 75,000,000 cubic feet per month. He was informed that 5000 cubic feet of gas was roughly the thermal equivalent of a barrel of fuel oil. If the value of fuel oil be taken at 80 cents and the cost of collecting gas—including depreciation of pipe-lines, gas traps, etc., and compressors' expense—at 3 cents per thousand, this involved a write up in value of nearly $10,000 per month; which would almost certainly result in increasing the cost of drilling by a $1.00 or more per foot. As in most questions of principle, there was room for two views, but he was inclined to believe that the cost of drilling should reflect the great additional expense in drilling an "outside" location—that is, outside the range of the gas supply—resulting in the consumption of perhaps $2000 or $3000 or more for fuel oil; but once a market were established for gas, this argument would be discounted.

In conclusion, the speaker said that he thought that it was very significant that the members of this Institution should elect to have a paper on this subject read to them. Times had changed since he first came out to Trinidad. The advances in the technology had introduced a bigger percentage of men with scientific training into the industry; they had brought their critical and analytical faculties to bear on the subject of costs, and the accountants' figures must now, therefore, bear the light of day. No costing system could be installed without the assistance of the technical men, neither could it continue to run without aid from them in the matter of allocations and distributions, and unless they were interested in and used the figures computed by the accountant, then all the time and labour required for accurate costing was wasted. And this, he knew, was far from being the case.

Mr. E. Cunningham Craig said that at one time after the war he had an interest in the question of "all-in" costs. Some of the companies found themselves in the position to pay dividends, and immediately the point arose: How much dividend should the oil companies in Trinidad be allowed to pay before they became liable for Excess Profit Duty? At that time all the companies exploiting oil in Trinidad agreed to combine, and to have a case put before the Treasury Board, and the Counsel employed to act for all these companies was Mr. Douglas Hogg (now Lord Hailsham). It was decided that there should be three witnesses to appear before the Treasury Board—Sir Boverton Redwood, Mr. Alexander Duckham and himself—and they dealt with different aspects of the question. The speaker had to deal with the number of wells drilled, the area of land exploited, and the "all-in" costs of producing the oil, as well as of the sums gained by the selling of the oil. They might be perfectly sure that the companies concerned at the time did not minimize the costs. He fancied the "all-in"

costs included the cost of making tea by their typists in their London offices. Some interesting details were arrived at by comparing the sum gained for selling the oil with the cost of exploiting the land. He was able to tell exactly what it had cost every company to produce a barrel of oil. He was not going into those figures, because they were confidential, but he might say that some of the costs were very low. In fact, the best one was considerably less than one shilling per barrel.

There were two questions which the speaker desired to put to the author, viz. whether he could tell them what was the general average cost for Trinidad of a barrel of oil at the well-head, and the price of a barrel of oil f.o.b. He mentioned that to see how the costs compared to-day with the costs of the days gone by. Roughly speaking, what the average cost should be in Trinidad.

Mr. H. D. Fletcher said what struck him most was that there must be tremendous differences in the costs arrived at by the various systems of allocating charges.

When an operator gives his cost per foot, it conveys nothing unless his system of allocation is known, and it is then comparable only with operators who use the same system.

Whether some standard system of costing could be arrived at for the purpose of comparison the speaker did not know, but he imagined something could be done; he had in mind that contractors in England and elsewhere, when tendering for large contracts, must have a very close estimate of what their costs will be, otherwise they could not cut their tenders to such close figures, and these estimates must be based on the accurate costing of previous work.

Most of the drilling in the United States of America is done by contractors, so there must be some standard system of costing to enable them to arrive at competitive figures.

With regard to Mr. Cunningham Craig's question as to the cost per barrel of oil, the speaker did not see how that could be gone into unless it was known how much oil would be obtained.

One could only estimate the cost per foot of the drilling, and if the hole turned out to be practically dry, the cost per barrel would be tremendous.

He was of opinion that if companies with different systems of costing were asked to contract to drill a given footage, there would be tremendous variations in their estimates.

Mr. J. L. Harris congratulated the author on a very lucid explanation of an extremely abstruse subject. He wondered if this particular aspect of accounting was not unnecessarily abstruse; for he felt that accountants were inclined to introduce complications into costs.

The cost of drilling seemed to him to be essentially the summation of accounts directly under the control of the drilling superintendent.

If charges entered into this summation that were not absolutely controlled by the head of the department, it was, he submitted, more difficult to ascertain such data as the comparative competence of drilling superintendents and the economy or otherwise following on the introduction of new machinery and/or revised methods of operation.

He agreed with Mr. Bennett's criticism regarding the complication of

the system, and fancied that introduction of such charges as compensation for pollution and cost of bungalows tended to obscure the issue, as direct charges were probably the best standards of comparison.

Mr. J. Mowll expressed his appreciation of the author's paper. He said the author's opening statement struck him as rather extraordinary, he referred to : " In the technical literature, there are few, if any, text-books on costing for a producing oil company." He had checked up that statement with a comprehensive catalogue of books on cost accounting, and although he found one or more books on costing for most industries, there was nothing in connection with the production of oil. It seemed very strange that no costing authority had given his attention to so important an industry as oil, and he believed there was some definite reason for it.

Of course, if there were some book on the subject, it was probable that the reasons given for there not being one would be wrong. A certain authority on costing in general gave two main reasons why cost accounts should be kept. The first reason was, " To be able to regulate selling prices according to cost and to frame estimates and tenders without error." That seemed to him to apply mainly to manufacturers or producers in direct competition. In the case of producing oil companies, the price they are to receive for their product was usually fixed by agreement, or was on some specified basis with a regular purchaser. The second reason was, " To establish a standard of cost in detail so that the source of any fluctuation in cost may be immediately apparent." He suggested that, due to the number of variable factors in the oil production business, costing authorities had found this impossible. The factors governing the cost of drilling were good examples.

Mr. H. A. Harris, in replying to the discussion, said he would prefer to make a collective answer to all the questions that had been asked, because the answers to most would be the same. The reason for the system was, as stated in the paper, to group expenditure into two main headings, and the total cost of each heading was arrived at as outlined. Having got at the direct cost, it can be subdivided in any way to suit the requirements of the technologist. The direct charges were the items over which the various departments had control, and then there were the indirect maintenance and depreciation charges, over part of which they had control —maintenance. They had no control over depreciation. It was a figure which had to be disposed of and brought into true cost, and having got to the working cost, the remainder of the expenditure could be dealt with in any manner one liked. In the particular system it was lumped on pro rata to the total working costs and the final totals, being of interest and value to the management and the board. Then one could go back and segregate those items which were of interest to the management, and information could be provided for the drilling superintendent, geologist or any other department. The drilling superintendent is advised from day to day of the wages, materials and shopwork charged to his department.

With regard to Mr. Cooper Scott's reference to direct cost, such cost could be divided in any manner desired. In the particular system the

allocation of direct charges was done by the department concerned, and not by the accountant. The accountant consulted its wishes.

The fluctuations in overhead charges were a separate item entirely, and are controllable by the board or by the management, and the fact that they were added to wells' cost was merely of interest in a producing field. That field was drilling wells and producing oil, and that field had expenses, and it was only fair in the final results that each of the two headings should bear their proportion of those expenses.

As had been pointed out, there were many ways of making a charge for plant. The method given in the paper was that capital accounts should be written down at suitable rates on the diminishing value, to which was added all maintenance and replacement of parts, and they were disposed of at the end of the accounting period. A time basis might be fixed, and it would develop into a rent charge. The entire depreciation on plant must be brought into account in arriving at the plant charge for drilling, and as long as the costing was in line with practice it would give one a very true figure. To take an extreme case. One man might buy a new rig every year. He might do that for ten years, and knew exactly what his costs were. Another man might buy one rig and run it for ten years; he also would know exactly what his costs were. So long as the costing for plant was in line with practice, it gave the true results, and the method adopted, as he had said, was writing down on the diminishing value, which was a very fair way of doing it, and it did provide over a period of years for bringing in the total expense on plant.

Mr. Bennett remarked that the system was suitable for a prosperous company. The author did not see the reason really for that remark. The object of his paper was to outline a method of costing drilling as had been practised, and no matter whether the company was prosperous or not, drilling costs were one thing, and making profits another. One could not get away from what it costs to drill, no matter how one's cost was compiled. So that whilst that system had been adopted in the case of a company which happened to be prosperous, there was no reason why the system, possibly with certain modifications, could not be adopted to give the true cost.

On the point of rents, in the author's view property rents and royalties were not charges against drilling nor against production. One company might elect to raise money to buy property, another company might prefer to pay rents. He agreed that rents and royalties did not constitute costs, and the rents mentioned in the paper were merely minor rents, not rents of property.

There was also the point of charging for the company's equipment following the charge for rents on tools borrowed. All tools—in that particular instance, all drilling plant—was in one capital account, and in a lump sum to cover the whole, with a suitable depreciation rate to cover the useful life of the whole material. He thought it was hopeless to keep track of every pump, engine or tool. One might reckon that there were so many boilers which would last so many years, and fix the rate of depreciation arbitrarily. Of course, it might happen that one boiler might fail in its first year, while another might have a very long life, but the whole cost would come out on average.

With regard to the charge for gas fuel, it was the aim when the system was first started that the cost of wells should be the full cost; therefore it was decided to charge for the gas used at the value of oil fuel, purely for the purpose of keeping their costs per foot comparative. As to whether it was correct in principle was debatable and a matter of opinion.

He was sorry it was not possible to give Mr. Cunningham Craig the costs he asked for, but the author believed that the general average figures for Trinidad were contained in Sir Thomas Holland's report of a few years ago on the Oil Industry of Trinidad, and the author thought that, with a small discount, those figures might represent the present-day ones. He was not refusing to give the figures, but the fact was he had forgotten what they were.

MR. CUNNINGHAM CRAIG: Did Sir Thomas Holland quote "all-in costs" for the industry?

AUTHOR: Yes, it was "all-in cost."

Continuing, the author said Mr. Fletcher had raised the point about comparison of cost. He was afraid if accountants were thrown together for the purpose of standardizing a method of costing it would develop into a dog-fight.

He might say again that the object of his paper was to set out what is included in the cost of a well, and it was just their opinion; probably many people did have quite different opinions.

With regard to geological expenses, he personally thought that the geologist was very closely connected with drilling, and his time and expense should be charged to that account, and the author also thought the geologist has got something to do with production. Presumably, he is the man to spot the well, therefore if the geologist had got to do with those headings, his salary, bonus, building allowances, bungalow maintenance should be charged to them.

He thought that the allocation of such overheads to drilling and production could be supported by the fact that in any new field or in any new factory or industry all preliminary expenses would be charged to capital account until production started.

Mr. Lonsdale Harris had raised a point that the costing system was extremely complicated. That was what they thought sometimes, but having arrived at their totals—they arrived at the direct cost first, of course, then go for the other one afterwards—they supplied the drilling superintendent with all the details he wanted. If he wanted to know how much lubricating oil was used, he saw, as a matter of routine at the end of any given period, the same as he saw his time sheets daily, but at the end of the month, or when the well was finished, they gave the direct cost sub-divided as the drilling superintendent wanted it.

With regard to office expenses, he took it that the accountant was there on a producing oil-field for the two main objects, and his time should be divided between the two.

Before closing the meeting, the CHAIRMAN remarked that the suggestion made by Mr. Fletcher would be very well worth following up. The matter

did not seem to him to present any insuperable difficulty. Having arrived at one method of costing, one should not have any difficulty in comparing costs. As matters stood, one was informed that it cost one company $5 a foot and another company $7 a foot, and these figures must be amended to make them truly comparative according to the methods adopted in allocating such costs. It seemed to him that once you came out in the open on the actual cost of drilling as computed by the various companies, there was no reason at all why figures should not be compiled to make comparisons, and he thought it would be of inestimable value to the operatives here.

He concluded by moving a vote of thanks to the author for reading his paper, and to the Apex (Trinidad) Oilfields, Ltd., for the use of the Club that night.

COAL AS A SOURCE OF LIQUID FUEL.*

By R. Lessing, Ph.D., F.I.C.

In discussing the potentialities of the methods available for the production of liquid fuels from coal, attention is usually focused on the process side, and insufficient consideration is given to the material itself and to the distinctive properties of its many varieties. It seems reasonable to postulate that the technical and economic soundness of schemes for using coal or its products in fluid form and the success of particular forms of treatment likely to ensue, can be assessed only if the existing knowledge of coal constitution is taken into account and the gaps in this knowledge are filled by more intensive investigation.

The enormous strides made in the utilization of oil fuels since the beginning of the century are due to :—

1. The facility of forming intimate mixtures of fuel and combustion air by vaporization of volatile hydrocarbons, and by the dispersion as spray droplets of heavier oils, in such a manner that rapid and complete combustion of the fuel is reached.
2. The ease and cleanliness with which liquid fuels can be handled and conveyed in closed pipe systems.
3. The high calorific value of liquid fuels which consist essentially of carbon and hydrogen and, with the exception of tar products and alcohols, do not contain oxygen which diminishes the calorific value.
4. The absence or negligible content of incombustible inorganic constituents.
5. The high potential heat content in their bulk and its ready divisibility, essential conditions for automotive purposes.

Against these obvious advantages must be put the absence of appreciable home supplies, at any rate in the countries of Western Europe, and the need for providing conveying and storage facilities in form of tanks.

Rapid and complete burning can be achieved still more readily with combustible gases, but their use is restricted to fixed points of production or pipe distribution systems.

Solid fuels cannot claim the above-mentioned advantages, with one exception. Coal can be burnt rapidly and completely if it is in the form of particles fine enough to be blown by air into combustion chambers very much like atomized fuel oil.

Pieces of coal, coke or wood, on the other hand, cannot be burned instantaneously, but must be exposed to passing currents of air for considerable periods of time, until they are consumed layer by layer. The wide difference in size of pieces or particles of most commercial varieties of coal involves

* Paper presented for discussion at the One Hundred and Seventieth Meeting of the Institution of Petroleum Technologists, April 6th, 1936.

the burning away of the smaller pieces before the larger ones are completely consumed. In consequence, the interstices between the pieces in a fuel-bed at rest change in volume as combustion proceeds, with a consequent modification in the local velocity of the air currents passing through the bed. The rate at which combustion proceeds around the individual pieces in the fuel-bed varies, therefore, considerably according to the free space at any point and at any given time, and so does the resistance offered to the air in the irregular and tortuous passages between the pieces. The phenomena in the fuel-bed are thus governed by aerodynamic laws, and these are of a much more complicated character than those applying to the relatively homogeneous mixtures of coal dust or oil spray dispersed in the combustion air.

The disposition of coal on chain grate stokers differs in this regard little from fuel-beds at rest; but the conditions are somewhat altered towards a more even flow of air through the layer when the coal is subjected to a rocking or other motion which effects a continual rearrangement of the pieces.

Added to these mechanical conditions are the complications brought about by the chemical and physical changes which coal undergoes during combustion and the carbonizing stage preceding it, as well as the interaction at high temperature between the different types of ash components left as residue. Moreover, coals, by reason of their specific ignitibility, reactivity, caking property and other characteristics, differ very widely from each other in their behaviour during the stages leading up to complete combustion, and the commercial varieties themselves consist of components or groups of constituents which in their turn show very marked differences.

The complexities of coal composition and utilization are referred to by way of explanation, and must not be exaggerated, for coal is, and is likely to remain, by far the largest source of energy. Therefore, fuel technology during the rise of the industrial era, until the appearance of oil, was developed almost exclusively on the basis of coal, and must continue to depend on it as its principal material.

These general principles underlying the various uses of coal as a fuel must be appreciated for a thorough understanding of the reasons which make its conversion into liquids desirable. The complexities of the composition and behaviour of coal alluded to in connection with its direct combustion become still more accentuated, when coal is to be used as a raw material for conversion into other products, and, in particular, into liquid fuels of different types. Success in this direction can be achieved only if the constitution of coal and its components is elucidated to a much greater extent than has been possible hitherto. Reactions as sensitive as those applied in these conversion processes, such as thermal decomposition of large organic molecules or synthesis by the addition of hydrogen to such molecules or their decomposition products, would in other branches of chemical industry presuppose a precise knowledge of the raw materials to be dealt with.

In the case of coal, such knowledge of the desired degree of precision is non-existent. The chemistry of coal was, until well into the present century, restricted to certain tests performed on commercial samples which, although useful in the characterization of general types, could not be considered as giving more than indices of a limited number of properties

of materials which were invariably highly heterogeneous mixtures. Modern coal research began in the immediate post-war period with the recognition of the difference in many respects between the four principal petrological components in ordinary bituminous coals. This sub-division constituted an important step in disentangling some of the factors which remain obliterated when applying only the customary methods of coal analysis. Although this division into the now well-known Stopes components, vitrain, clarain, durain and fusain was not intended to mean more than a first rough classification of any coal into four rock types, it formed the stepping-stone for a vast amount of fruitful investigation during the last fifteen years.

In order to appreciate the significance of coal constitution, it is important to visualize its original vegetable raw material and the mode of its transformation by biological, chemical and geophysical agencies, since any reactions to be carried out with the coal as we find it must set in at the stage where the natural process of coal formation has been arrested. Whatever the original vegetable deposit from which each of the rock-types is derived, " coalification " was accompanied by the loss during geological periods of oxygen, hydrogen and some carbon, in form of water, methane and carbon dioxide, whereby a gradual concentration of carbon was effected through the stages of peat, lignite and the range of bituminous coals to anthracite. The stage to which this " carbonization " at low temperatures—not exceeding 200° C.—has proceeded determines the rank of coal, *i.e.* the ratio of carbon : hydrogen : oxygen.

From the point of view of chemical and thermo-chemical treatment and of direct fuel value, the rank of coal is all-important. Generally speaking, the higher the rank, the higher is the calorific value ; and the lower the rank, the higher is the reactivity towards chemical combination, be it ignitibility or combustibility by reaction with oxygen as in combustion, ease of reduction or combination with hydrogen as in hydrogenation, or thermal decomposition without added reagents as in carbonization. Hence it has been found that brown coals (low rank) are more readily amenable to hydrogenation than bituminous coals.

The rank of coal and all it implies is established by ultimate analysis ; it therefore gives only the elementary composition, and does not permit an insight into the constitutional structure of the chemical compounds contained in the coal magma. The great object of coal research is to establish this constitution. So far it has not been possible to do more than to divide the coal substance or that of its rock-types into groups of compounds of typical properties, by such methods as fractionation with solvents, mild oxidation, chlorination, progressive distillation and thermal decomposition over long periods at low rates of rise of temperature and the examination of the reaction products. The groupings found show considerable differences between vitrain, clarain, durain and fusain. These components can now be separated with tolerable ease and certainty by density methods, the friable charcoal-like fusain having been previously removed by screening or elutriation. Even in these components the chemical groups are not homogeneously distributed ; for they are still conglomerates of plant entities or residues, visible under the microscope and embedded in a structureless matrix or ground-mass. In the extended Stopes classification, now adopted by international agreement, each of the four rock-types is further sub-

divided into "macerals," which are microscopically recognizable units of transformation products of the original vegetable material.

The development of a technique of identification and isolation of the morphological elements of the coal mass is one of the immediate practical problems of coal research, for it would enable the chemist to deal with substances a little nearer the pure stage than the nondescript mixtures to which his analytical skill is at present confined.

These considerations of the constitution of coal refer only to its organic portion. The inorganic constituents are likewise of vital importance in any phase of coal utilization, and not least in its conversion into liquids. As far as the accessory mineral impurities are concerned, methods for their complete elimination are now available, and it is only a question of time for processes of high cleaning efficiency to become the general practice in coal preparation. The "inherent" ash, however, which cannot be removed by existing methods, presents problems of more than academic interest. The author directed attention to the catalytic influence of inorganic substances on the thermal decomposition of coal in 1914, and in greater detail in 1924. Industrial developments have proved the accuracy of this prediction, both in carbonization and even more forcibly in hydrogenation. A close study of the mineral constituents of coal and their modification by elimination or addition is therefore essential for success in these treatment processes.

Coal as a material has been dealt with so far rather than the methods by which this solid can be transformed into liquids. This has been done advisedly, for whilst the technical and economic aspects of the different processes have been considered frequently and exhaustively during recent years, the substance to be treated, its properties and suitability for various modes of liquefaction have received relatively little public attention.

It is not proposed within the compass of this summary to describe individual methods of converting coal into liquids, but merely to touch on some of the fundamental principles involved.

In carbonization the coal is subjected to a number of reactions of dehydration, dehydroxylation, dehydrogenation, autoxidation, and scission of carbon compounds.

These reactions overlap each other in various ways :—

1. The different molecular compounds in the coal components are susceptible in different directions and degrees to the attack by heat.
2. Heat is applied so rapidly that the reactions overtake each other, and do not occur successively and in orderly fashion.
3. Primary decomposition products are subjected to secondary decomposition.
4. Tar and pitch formed primarily in one part of the carbonizing vessel modify the properties of raw coal in another part.
5. Reduction of carbon dioxide formed by the action of the oxygen present in coal on carbon and by the water gas reaction.
6. Side reactions occur with minor constituents, such as sulphur, nitrogen and inorganic compounds.

The result of this involved interplay is the tendency to decompose the coal substance into solid carbon (coke) and gas, leaving as products of partial decomposition, pitch, tar oils and light hydrocarbons, which, owing to rapid

withdrawal from the heating zone, have escaped decomposition. The behaviour of different types of coal on carbonization has been studied extensively, although much work remains to be done in the elucidation of individual phases of the problem.

The principles involved are the same whether carbonization is carried out at high temperature of say 1000° C., or at " low " temperature of say 600° C. The effect of operating at the lower temperature is to preserve the tar from the degree of decomposition to which the higher temperature exposes it. In consequence, both yield and character of tar are different. At high temperature the tar yield is about 5 per cent., and at lower temperature up to 10 per cent. The former tar has a high pitch content, and its hydrocarbons are mainly aromatic. The latter has a low pitch content, a high percentage of phenolic bodies, and its hydrocarbons are paraffinoid.

In hydrogenation the far-reaching decomposition to coke is avoided, and the conversion of more than 60 per cent. of the coal into motor spirit is made possible, partly by the application of pressure (say 250 atm.), whereby the equilibrium of drastic decomposition is not attained, partly by the relatively low temperature of about 450° C., and lastly, but not least, by the reduction of oxygen compounds by hydrogen and the addition of hydrogen to the coal substance. Details of the hydrogenation of coal and coal-tar oils have been given frequently during recent years, and the brilliant achievement of Imperial Chemical Industries, Ltd., with the large installation at their Billingham works has proved its technical success in the treatment of British coal. Its general application again requires the closest possible study of coal constitution and the selection of the most suitable kinds for treatment.

Catalysis has made possible yet another way in which liquid fuels can be obtained from coal. In the Fischer–Tropsch process water gas generated from coke and enriched in hydrogen so as to contain 2 parts of hydrogen to 1 part of carbon monoxide by volume, or coke-oven gas treated to give the same composition is, after the complete elimination of sulphur, passed at atmospheric pressure over a catalyst of nickel–aluminium–manganese on kieselguhr at 190–210° C. A yield of 100–120 grams of motor spirit per cubic metre of " synthesis " gas is obtained.

The methods so far discussed have as their object mainly the production of motor spirit; for the heavier portions of coal tar and L.T.C. tar, so far as they are not submitted to hydrogenation or cracking, do not enter the fuel market to a great extent. This is largely due to commercial considerations, since technically tar oils can be produced to form a usable fuel, certainly for furnace firing, and they can be treated for use in internal-combustion engines, at any rate of the slow-speed diesel type. Generally, the production of diesel oils from coal is a problem which has not yet been solved, or perhaps—for economic reasons—not yet seriously attempted.

The desire to burn coal in liquid form has, ever since the war, caused proposals to be made for the suspension of pulverized coal in oil for the direct firing through liquid fuel burners of oil–coal mixtures. The difficulty yet to be overcome is to confer reasonable stability and viscosity on such mixtures, two somewhat incompatible conditions. The use of stabilizers presents technical and economic objections. Work on the colloidal dispersion of the coal substance has shown that certain solvents can bring a large

proportion of suitable coals into permanent solution, and the possibility is foreshadowed of effecting this result with a wider, though not unlimited range of oils, if the mixture is subjected to high pressure at elevated temperature.

To this class of processes belongs the extraction of coal by tetralin or a mixture of tetralin and cresol, whereby after removal of the solvent a pitch-like residue is obtained. It is claimed that when this coal extract is subjected to hydrogenation, the results are superior to those from the direct treatment of coal.

It is obvious that oil–coal mixtures, although being fluid, and thereby sharing the advantages of liquid fuels, cannot be expected to form direct substitutes for them for all uses. If it is considered that, say for diesel use, even petroleum oils must be carefully selected and prepared, it will be apparent that products having a high mean viscosity, a heterogeneous chemical composition and containing some ash, will call for the special construction of suitable furnaces and engines in which they can be consumed efficiently. However, seeing that experiments on the more difficult problem of direct combustion of dry coal dust in compression-ignition engines show some promise, and remembering that the mechanical stoker was developed to burn low-grade coal which could not be handled on the old type of grates, the possibility of progress in this direction should not be overlooked.

Development in the conversion of coal into liquid fuel during the last decade has proceeded steadily, and progress is now being accelerated in some countries. In Germany, for instance, the annual capacity of plants in operation, under erection and projected is stated to be approaching 1,000,000 tons of motor spirit. For reasons of national economy and safety it is to be expected that all coal-producing countries will pay increasing attention to the problem of gaining the advantage of fluidity for at least a portion of their supply of indigenous fuel.

LIQUID FUEL FROM COAL OBTAINED BY LOW-TEMPERATURE CARBONIZATION.*

By W. A. Bristow, M.I.E.E., M.I.A.E., F.R.Ae.S.

The production of oil from coal by carbonization at low temperatures had at one time little importance. The main object in view was the manufacture of smokeless fuel, and in those days oil products were not so important as they are now.

In the main specification of Thomas Parker (No. 14365 of 1906) the first paragraph reads :—

> "This invention relates to the production of fuel by the partial destructive distillation of coal at low temperature, whereby a fuel is produced of uniform composition and of high calorific value whose combustion in an open fire grate yields a high temperature and is practically smokeless, and whereby also in the process of its production gas, tar, and ammonia are yielded, so that thus the cost of production of the fuel is such as to allow of its ready sale on the market."

The simple mention of the one word "tar" is in striking contrast to some of the various claims we have read in other specifications in the last few years. This tar was, and is to-day, merely a by-product of the process, and if it were not for the economic soundness of the coke side of the business, it would be quite impossible to work at a profit.

In the year 1928, in order to distinguish this tar from the high-temperature product, we gave it the name of crude coal oil, by which it is now generally known. In theory its production is quite simple.

Bituminous coking coals are heated at temperatures below 600° C. for four hours, and the volatile matter which is driven off is condensed and collected. The amount driven off depends on the volatile content of the coal, the temperature to which it is heated, and the time it is subjected to the heat.

Statements to the effect that large yields of liquid products can be produced from ordinary bituminous coals by some mysterious complications in the process are not based on fact. Any schoolgirl can obtain the maximum yield by heating the coal in an old kettle and condensing the products issuing from the spout.

One method of carrying out the process on a commercial scale is as follows :—

The gaseous and liquid products evolved from the coal charge in the retorts, pass, via the water-cooled offtakes, into the hydraulic main, where most of the heavier hydrocarbon vapours and a large quantity of the ammonia liquor are condensed. The oil and the ammonia liquor condensed pass through tar towers situated at the end of each hydraulic main,

* Paper presented for discussion at the One Hundred and Seventieth Meeting of the Institution of Petroleum Technologists, April 6th, 1936.

the object of the towers being to keep the hydraulic main free from deposits of heavier tarry matter. From the towers the crude oil and liquor pass to a decanting tank, where separation of oil and liquor takes place so effectively that the crude oil passing to storage contains less than 3 per cent. of water.

The gas and uncondensed liquid products leave the hydraulic main at a temperature of about 85° C., and pass direct to electrostatic tar precipitators, the function of which is now well known. The tar or oil in the gas is precipitated from the gas due to the action of an electrical discharge of 50,000 volts D.C.

The gas leaves the precipitator free from visible oil particles.

On leaving the precipitator the gas passes through steam heaters, the object being to heat up the gas to prevent condensation of light oil vapour in the sulphuric acid washers, into which the gas now goes forward.

The washers are in the form of a section of fractionating column, with trays and bubble caps. There are three trays in each absorber, and the gas bubbles through the caps, which are sealed in sulphuric acid. The ammonium sulphate solution so formed is passed to evaporators, where the sulphate of ammonia crystals are deposited. The crystals are separated, dried, neutralized and weighed into sacks.

The gas leaves the acid washers at 80° C., and enters the water-cooled condensers, which it leaves at a temperature of 20° C. All liquid products which are condensed from the gas up to this point are transferred to the aforementioned decanting tank.

From the condenser exit, the gas is passed through the exhausters and on to a final cooler, where the temperature of the gas is further decreased, to about 11° C., in order to obtain maximum efficiency in the crude spirit extraction plant which follows.

The cold gas passes up two scrubbers in series packed with wooden grids, down which a selected fraction of coal-oil distillate is circulated. The oil fraction extracts the crude spirit vapour from the gas, and from the oil the spirit is recovered by steam distillation, the oil being cooled and used again for further extraction in the scrubbers.

On leaving the scrubbers the gas passes to a gasholder, from which it is returned to the plant for heating the retorts and for other process work requiring supplies of gas.

The resultant crude oil has the characteristics shown in the specification appended.

As will be seen, the crude, unlike high-temperature tar, is of low specific gravity, is very fluid and it has a reddish-brown colour. The yield per ton of coal is about 18–20 gallons per ton—that is, from ordinary bituminous coal having a volatile content of about 36 per cent., and leaving the residual fuel with about 10 per cent. of volatiles.

A typical weight balance is as follows :—

	Cwts./ton.	Yield, %.
Coal Oil	2·00	10·00
Liquor	2·15	10·75
Gas	1·85	9·25
Residual Fuel	14·00	70·00
	20·00	100·00

The yield of crude spirit from the gas is slightly in excess of 3 gallons per ton of coal.

Much higher yields of oil and spirit could be obtained from some cannel coals, but these are not used, as the coke therefrom has little value. When considering claims for high yields, it is essential to know whether or not cannel coal was used for the test. As much as 80 gallons of oil has been recovered from one ton of cannel, but the solid residue is practically useless.

The hydrocarbons of low-temperature crude oil are more closely related to petroleum than to the hydrocarbons of high-temperature tar, and, confirming this, it may be pointed out—

1. That the low specific gravity of the lower-boiling hydrocarbons indicates a high hydrogen content, agreeing in this respect with petroleum.

2. That the paraffin wax of the high-boiling portions of low-temperature tar is found in petroleum, but not in high-temperature tar which contains anthracene instead.

3. That low-temperature crude contains no recoverable naphthalene, and only in isolated cases does petroleum contain naphthalene.

Low-temperature crude contains a much higher percentage of phenolic bodies (generally known as tar acids) than does high-temperature tar. It was at one time considered that these were more or less valueless, on account of the absence of true phenol, and the fact that they consisted chiefly of the type known as high-boiling tar acids together with some cresylic acid.

It is now true, however, that these tar acids are in great demand, particularly for the manufacture of commercial disinfectants. Such tar acids have a very high germicidal value, and, made up in the form of commercial products, are being exported to every part of the world.

It is not proposed, however, to deal with the tar acid branch of the subject in this short summary of the work.

The nature of the crude oil is largely dictated by the coal from which it is made, and the temperature to which it is heated, and the same factors determine the quality and burning properties of the coke. It has been found by long experience that the temperatures at which we work are the best for the coke, and we have therefore had to design a plant and process that would enable this temperature to also give us the best possible oil and spirit. This we have done, and to-day we could not make better liquid products whatever temperature we used.

It is interesting to note that the total time of coal distillation by the "Coalite" process is only 4 hours, one retort does six charges every 24 hours for 365 days per year. This is very much quicker than most processes, some of which require 24 hours in the retort.

The question of temperature control is most important, and the heat must be maintained within very fine limits. Recording pyrometers are installed with each retort, and the temperatures are taken both at the top and the bottom. It is also important to maintain, as far as possible, uniform coal specifications, as differences give rise to variations in the products, which may have to conform to strict contract specifications over long periods.

In the years 1927 and 1928, when the present works began to get into production, the crude oil was sold, but the Company had no information

as to the purposes for which it was used. It was found out afterwards that it was being mixed with high-temperature creosote and exported to America, but the large increase in the proportion of low-temperature crude made itself apparent to the American importer, and this branch of the business terminated in twenty-four hours. In the meanwhile, the Company had been erecting its own distillation plants which happened to be ready about the day before the usual method of disposal terminated, thus most fortunately avoiding what would have been a very serious setback. Distillation began along fairly simple lines, the product being divided into four portions—light, middle and heavy oils, and pitch. In a schedule accompanying this paper are given the distillation ranges of the three liquid fractions. The specifications must be studied to be understood as, owing to the oil being distilled in pot stills, there is a great deal of overlapping with the fractions. This method of distillation is being abandoned in favour of vacuum distillation, which will give much better results. Sufficient to say that the light oil is 65 per cent. at 200° C., middle oil mostly comes over between 200° C. and 260° C., and heavy oil mainly between 260° C. and 360° C. In the early days these fractions were mainly sold for their tar acid content, and the neutral residues were mostly used as fuel, and were sometimes difficult to dispose of.

The imposition of a duty of 1*d*. per gallon on imported fuel oil turned the Company's attention to the possibilities of making a suitable fuel oil fraction, and after some difficulty a fuel oil was produced which complied with the Admiralty specification, as shown in the attached schedule. The first bulk consignment of this oil was sent to the Admiralty in December 1932, and the subsequent trials at sea were fully reported on in the paper read by Engineer-Captain Dunlop, R.N., before the Scottish Engineering and Shipbuilding Institution. In preparing fuel oil to the Admiralty specification, all the crude tar acids were removed; but in other fuel-oil specifications they were retained, as will be seen in the schedule. Large quantities of these fuel oils were sold, and gave complete satisfaction.

Attention was next directed to the preparation of low-temperature creosote, and after a great deal of work the British Standards Institution included the low-temperature product in their Standard Specifications. Large quantities of low-temperature creosote have been sold in this country and also shipped abroad.

The possibility of producing a suitable diesel oil from the middle and heavy fractions was then investigated, but this proved to be an exceedingly difficult matter. It was easy to make a diesel engine run after a fashion on a carefully prepared fraction of the distillate, but starting was very difficult, due to the high spontaneous ignition temperature of all coal oil distillates and the presence of bodies that tended to choke the nozzles after prolonged running.

An experimental plant was installed nearly a year ago, with two variable-compression diesel engines and all the plant necessary for the preparation of the diesel fractions, and considerable running has been carried out, including 100-hours' runs similar to those required for aviation engines. Before putting down this plant a number of tests were carried out on engines kindly supplied by Messrs. Ruston & Hornsby at their Works at Lincoln, the results of which were published about November 1934.

Most of the difficulties of manufacture have been fairly easily surmounted by washing and redistillation, but the question of bringing down the spontaneous ignition temperature without lowering the flash point has proved extremely difficult. The problem, however, has now been solved, and it is confidently expected that there will be no more trouble on this account.

After extensive bench tests the oil was tried on a 32-seater coach—A.E.C. "Regal," No. L.J. 8798, fitted with an A.E.C. Ricardo six-cylinder diesel engine, bore 115 m/m–142 m/m (8850 c.c.), having a compression ratio of 16 : 1, and developing 140 b.h.p. at 2500 r.p.m. The engine was fitted with a Bosch fuel pump and Bosch injectors, and was also fitted with a heating plug for starting. The coach was on the regular daily passenger service between London and Bournemouth, and on December 11th the coach performed the return journey without incident. The tank and autovac were drained, and thirty gallons of oil were carefully measured into the tank and autovac, and the plugs sealed with a lead seal. One driver took the coach down in the schedule time of five hours, and No. 2 driver left Bournemouth at 2.40 and reached King's Cross at 7.30. No. 1 driver, on being asked, expressed the opinion that the fuel gave plenty of power, and that at speeds above 30 m.p.h. the engine ran as well as with the normal petroleum fuel, but that at speeds below 30 m.p.h. he was inclined to think that it was perhaps a little more noisy. No. 2 driver expressed the opinion that he could not notice any difference from his normal fuel, except that the exhaust at some speeds was perhaps a little more pronounced and lighter in colour. The total distance covered was 225 miles, and the fuel injection valves, on being withdrawn, were found to be quite clean.

Other running tests have been since carried out with equally satisfactory results, and the oil is still being improved. It is estimated that about one third of the total crude will be available as diesel oil.

It is sometimes stated in claims made for new processes that the whole of the oil being obtained from the coal is in the form of diesel oil, but such cannot be the case. The oil must first be free from pitch, tar acids, and other deleterious constituents, and must be treated in order to reduce the spontaneous ignition temperature. The dope used on the Bournemouth run formed approximately 2 per cent. of the total oil.

In addition to its use as diesel oil, the low-temperature crude can be converted into motor spirit by hydrogenation, and it is particularly suitable for this purpose. The yield is about 100 per cent. by volume, and the oil is very easy to manipulate. In addition to the work carried out by the Imperial Chemical Industries in this direction, the Fuel Research Board have also done a great deal of most valuable work, which is likely to be extensively developed on a commercial scale in the future. At the Fuel Research Board the low-temperature crude is mixed with hydrogen at a pressure of about 200 atmospheres and a temperature of 450° C. The mixture is then passed through a catalyst consisting of molybdenum sulphide disposed on an inert material such as silica gell. The process works without any difficulty. The crude oil has only to be passed through once, and there is a yield of 100 per cent. by volume.

Finally, with regard to the crude spirit which is scrubbed from the gas, a refining method has now been worked out, and the finished product is giving very satisfactory results.

Specifications of the crude and the motor spirit as supplied to the Air Ministry will be found in the appendix.

The problems in connection with the preparation of a spirit to Air Ministry standards are many and difficult. They have all been overcome. The octane number, distillation range, sulphur content and gum growth requirements are all satisfactorily met, and the spirit has taken its place as a normal Air Force supply. It is also eminently suitable for automobile engines, and large quantities have been distributed through No. 1 pumps during the past few months.

To sum up, therefore, it is perhaps fair to claim that during the past few years we have demonstrated that these different oils and motor spirit can be made from coal and at a profit. The Company has made and marketed more than 150,000 tons of these oil products, and has no difficulty whatever in making them to conform to established specifications with complete uniformity and regularity. What was shortly referred to by the late Mr. Thomas Parker as "tar" has expanded into a considerable industry of great national importance, and there is no reason why it should not be developed to a very much greater extent during the next few years.

We cannot expect to produce sufficient oil to supply all our own requirements, and it is a great disservice to the low-temperature industry to make any such rash claims. Likewise, those responsible for this new business have no thought or intention of embarking on any widespread system of distribution, being more than content to work through the existing machinery, providing that the products do, as far as possible, reach the public with such a name as will indicate that they are home-produced oils. It is only right that the coal-oil industry should secure their measure of goodwill in this important field.

We have, of course, received a great deal of assistance in the development stage, and among others I should particularly like to mention the Mines Department, the Department of Scientific and Industrial Research, the Fuel Research Board, and Professor Morgan, all of whom have given very valuable assistance and encouragement.

APPENDIX.

Crude Coal Oil.

Specific Gravity at 60° F.	1·03
Water	1·85%
Closed Flash Point (Pensky Martin)	123° F.
Open Flash Point (Pensky Martin)	166° F.
Fire Point (Pensky Martin)	204° F.
Viscosity at 70° F. (Redwood No. 1)	365 seconds
Viscosity at 100° F. (Redwood No. 1)	112½ seconds
Crude Tar Acids, Dist. to 360° C. (Standard Method)	39·06%
Crude Tar Acids, Calculated on Crude Oil (Standard Method)	23·50%
Initial Boiling Point	100° C.
Final Boiling Point	360° C.
Ash	0·056%
Free Carbon (Insoluble in Benzole)	0·275%
Carbon Residue (Conradson)	3·34%
Calorific Value	16,858 B.Th.U./lb.
Sulphur	0·60%

Distillation Range.

Temperature.	%.	Temperature.	%.
Up to 110° C.	1·50	Up to 250° C.	32·00
120	2·50	260	35·50
130	3·50	270	38·50
140	4·50	280	41·00
150	4·50	290	43·00
160	4·50	300	46·00
170	4·50	310	49·00
180	5·00	320	51·50
190	6·00	330	53·00
200	8·50	340	56·00
210	12·00	350	58·00
220	18·00	360	62·00 (drained)
230	24·00	Residue	38·00 (by volume)
240	29·00		

"COALITE" LIGHT OIL.

Specific Gravity at 60° F.	0·9085
Water	1·20%
Closed Flash Point (Pensky Martin)	62° F.
Open Flash Point (Pensky Martin)	66° F.
Fire Point (Pensky Martin)	90° F.
Viscosity at 70° F. (Redwood No. 1)	32¼ seconds
Viscosity at 100° F. (Redwood No. 1)	31¼ seconds
Initial Boiling Point	86° C.
Final Boiling Point	310° C.
Crude Tar Acids (Standard Method)	26·20%
Ash (5-gm. method)	0·0080%
Carbon Residue (Conradson)	0·421%
Calorific Value	17,400 B.Th.U./lb.
Sulphur	0·92%

Distillation Range.

Temperature.	%.	Temperature.	%.
Up to 90° C.	1·00	Up to 210° C.	74·00
100	4·00	220	80·00
110	6·50	230	83·50
120	8·00	240	86·00
130	9·00	250	87·50
140	10·50	260	89·00
150	14·50	270	90·00
160	21·00	280	91·00
170	31·50	290	92·00
180	41·00	300	93·00
190	53·00	310	93·50
200	65·00	End point 314	94·00 (drained)

"COALITE" MIDDLE OIL.

Specific Gravity at 60° F.	0·9520
Water	1·00%
Closed Flash Point (Pensky Martin)	126° F.
Open Flash Point (Pensky Martin)	135° F.
Fire Point (Pensky Martin)	160° F.
Viscosity at 70° F. (Redwood No. 1)	38¼ seconds
Viscosity at 100° F. (Redwood No. 1)	33¼ seconds
Initial Boiling Point	101° C.
Final Boiling Point	312° C.
Crude Tar Acids (Standard Method)	41·20%
Ash	0·0060%
Carbon Residue (Conradson)	0·0960%
Calorific Value	16,924 B.Th.U./lb.
Sulphur	0·84%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 110° C.	2·00	Up to 220° C.	65·00
120	2·00	230	73·50
130	2·00	240	79·50
140	2·00	250	83·50
150	2·50	260	87·00
160	2·50	270	89·00
170	3·50	280	90·00
180	6·00	290	91·50
190	15·00	300	92·50
200	36·50	310	93·50
210	53·00	End point 312	95·50 (drained)

"Coalite" Heavy Oil.

Specific Gravity at 60° F.	1·0090
Water	1·75%
Closed Flash Point (Pensky Martin)	161° F.
Open Flash Point (Pensky Martin)	192° F.
Fire Point (Pensky Martin)	233° F.
Viscosity at 70° F. (Redwood No. 1)	102½ seconds
Viscosity at 100° F. (Redwood No. 1)	56½ seconds
Initial Boiling Point	114° C.
Final Boiling Point	400° C.
Crude Tar Acids (Standard Method)	39·40%
Ash	0·0080%
Carbon Residue (Conradson)	0·160%
Calorific Value	16,604 B.Th.U./lb.
Sulphur	0·60%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 190° C.	2·50	Up to 300° C.	58·00
200	3·00	310	61·50
210	4·50	320	65·00
220	11·00	330	69·00
230	18·00	340	72·50
240	25·00	350	77·00
250	33·00	360	80·00
260	38·00	370	84·00
270	43·00	380	86·50
280	48·50	390	89·50
290	52·50	400	93·00 (drained)

"Neutral" Light Oil.

Specific Gravity at 60° F.	0·8465
Water	Nil
Closed Flash Point (Pensky Martin)	56° F.
Open Flash Point (Pensky Martin)	59·5° F.
Fire Point (Pensky Martin)	84° F.
Viscosity at 70° F. (Redwood No. 1)	31⅛ seconds
Viscosity at 100° F. (Redwood No. 1)	27⅜ seconds
Initial Boiling Point	100° C.
Final Boiling Point	324° C.
Crude Tar Acids (Standard Method)	Nil
Ash	Nil
Carbon Residue (Conradson)	0·125%
Calorific Value	19,300 B.Th.U./lb.
Sulphur	0·94%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 110° C.	0·50	Up to 230° C.	82·00
120	2·00	240	84·50
130	6·00	250	86·50
140	13·00	260	88·00
150	23·00	270	89·00
160	34·00	280	90·00
170	44·50	290	91·00
180	52·50	300	91·50
190	61·00	310	92·00
200	68·00	320	92·50
210	74·00	End point 324	94·00 (drained)
220	79·00		

"NEUTRAL" MIDDLE OIL.

Specific Gravity at 60° F.	0·8800
Water	Nil
Closed Flash Point (Pensky Martin)	120° F.
Open Flash Point (Pensky Martin)	123° F.
Fire Point (Pensky Martin)	158° F.
Viscosity at 70° F. (Redwood No. 1)	30½ seconds
Viscosity at 100° F. (Redwood No. 1)	29 seconds
Initial Boiling Point	152° C.
Final Boiling Point	318° C.
Crude Tar Acids (Standard Method)	Nil
Ash	Nil
Carbon Residue (Conradson)	0·135%
Calorific Value	18,900 B.Th.U./lb.
Sulphur	0·80%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 160° C.	1·50	Up to 250° C.	75·00
170	5·00	260	81·00
180	13·00	270	85·00
190	21·50	280	88·00
200	30·50	290	90·50
210	41·00	300	92·00
220	51·00	310	93·00
230	60·00	End point 318	95·50 (drained)
240	68·00		

"NEUTRAL" HEAVY OIL.

Specific Gravity at 60° F.	0·9650
Water	Trace
Closed Flash Point (Pensky Martin)	164° F.
Open Flash Point (Pensky Martin)	197° F.
Fire Point (Pensky Martin)	226° F.
Viscosity at 70° F. (Redwood No. 1)	51½ seconds
Viscosity at 100° F. (Redwood No. 1)	40½ seconds
Initial Boiling Point	184° C.
Final Boiling Point	400° C.
Crude Tar Acids (Standard Method)	Nil
Ash	0·01%
Carbon Residue (Conradson)	0·0972%
Calorific Value	18,200 B.Th.U./lb.
Sulphur	0·78%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 190° C.	—	Up to 300° C.	49·50
200	0·50	310	54·00
210	2·00	320	59·50
220	4·00	330	65·50
230	7·50	340	69·50
240	11·00	350	73·50
250	16·00	360	78·00
260	22·00	370	82·00
270	28·00	380	85·00
280	33·50	390	88·00
290	41·00	End point 400	92·50 (drained)

SPECIFICATION "E" OIL.

(Admiralty Quality Fuel Oil.)

Specific Gravity at 60° F.	0·9830
Water	0·30%
Closed Flash Point (Pensky Martin)	208° F.
Open Flash Point (Pensky Martin)	212° F.
Fire Point (Pensky Martin)	255° F.
Viscosity at 70° F. (Redwood No. 1)	81½ seconds
Viscosity at 100° F. (Redwood No. 1)	49⅝ seconds
Initial Boiling Point	207° C.
Final Boiling Point	400° C.
Crude Tar Acids (Standard Method)	2·50%
Ash	0·012%
Carbon Residue (Conradson)	0·597%
Calorific Value	18,275 B.Th.U./lb.
Sulphur	0·78%

Distillation Range.

Temperature.	%	Temperature.	%
Up to 210° C.	—	Up to 310° C.	43·00
220	0·50	320	49·50
230	2·00	330	57·00
240	5·50	340	62·50
250	7·00	350	68·00
260	11·00	360	74·00
270	15·00	370	79·00
280	21·50	380	83·00
290	28·00	390	87·00
300	35·00	End point 400	91·50 (drained)

SPECIFICATION "C" FUEL OIL.

Specific Gravity at 60° F.	1·0085
Water	0·20%
Closed Flash Point (Pensky Martin)	186° F.
Viscosity (Redwood No. 1 at 100° F.)	53·5 seconds
Distillation:	
Initial Boiling Point	182° C.
Distillate to 300° C.	72·0%
Final Boiling Point	377° C.
Crude Tar Acids	
Total	50·0%
Determined in Distillate to 360° C.	46·0%
Determined in Distillate to 315° C.	43·0%
Sediment	Negligible
Ash	0·0097%
Pitch Content (Admiralty Method)	2·18%
Carbon Residue (Muffle Determination)	1·25%
Calorific Value	16,848 B.Th.U./lb.
Sulphur	0·70%
Carbon Residue (Conradson)	0·440%

Full Distillation Range.

Temperature.	%	Temperature.	%
Up to 190° C.	1·0	Up to 290° C.	68·0
200	2·0	300	72·0
210	7·0	310	77·0
220	16·0	320	80·0
230	30·0	330	84·0
240	38·5	340	86·0
250	47·0	350	88·0
260	53·0	360	91·0
270	58·5	370	93·0
280	63·0	377	96·0

PITCH.

	Quality.	
	Standard.	Hard.
Twist Point (Standard Method)	45·5° C.	53·0° C.
K. and S. Softening Point	66·0° C.	73·5° C.
Fusing Point (Standard Method)	78·0° C.	88·0° C.
Volatile Matter (Standard Method)	81·50%	79·74%
Ash (Standard Method)	0·22%	0·24%
Free Carbon (Insoluble in Benzene)	12·10%	13·46%

LOW-TEMPERATURE CREOSOTE TO BRITISH STANDARD SPECIFICATION.

	Oil.
Specific Gravity at 38° C. (100° F.)	0·9940
Moisture	1·75%
Fluidity	Completely fluid at 38° C. and after standing 2 hrs. at 32° C.
Distillation 100 c.c. at 38° C.—250 c.c. flask:	
Up to 205° C. measured at 38° C.	1·80 c.c.
Up to 230° C. measured at 38° C.	18·30 c.c.
Up to 315° C. measured at 38° C.	65·30 c.c.
Residue	Soft, not sticky, 33 gms.
Crude Tar Acids in Distillate—315° C.	46·01%
Matter Insoluble in Benzene	Nil

"HITARAC."

(A Special Oil of High Tar Acid Content.)

Specific Gravity at 60° F.	0·978
Water	0·80%
Closed Flash Point (Pensky Martin)	125° F.
Viscosity (Redwood No. 1 at 100° F.)	37½ seconds
Crude Tar Acids	44·0%
Crude Tar Acids in Distillate to 315° C.	48·0%
Material Insoluble in Benzole	Nil
Ash	0·008%
Pitch Content (Admiralty Method)	2·29%
Calorific Value (Gross)	16,694 B.Th.U./lb.
Sulphur	0·78%
Carbon Residue (Conradson)	0·275%

Distillation Range.

Temperature	%	Temperature.	%
Up to 180° C.	2·5	Up to 280° C.	82·5
200	11·0	300	88·5
220	41·0	320	92·5
240	62·0	340	95·0
260	75·0	F.B.P. 357	97·5

Diesel Oil.

Specific Gravity at 60° F.	0·916
Closed Flash Point (Pensky Martin)	166° F.
Viscosity at 100° F. (Redwood No. 1)	31 seconds
Coke	0·08%
Ash	Nil
Cold Test at 0° F.	Fluid
Sulphur (Total)	0·91%
Mechanical Impurities	Nil
Water	Nil
Spontaneous Ignition (in Oxygen)	255° C.
Crude Tar Acids	Nil
Calorific Value (Gross)	18,450 B.Th.U. 1 lb
Calorific Value (Nett)	17,269 B.Th.U. 1 lb.

Distillation Range (I.P.T.).

Temperature.		Temperature.	
I.B.P.	165° C.	263	70
200° C.	10%	279	80
216	20	296	90%
222	30	F.B.P.	316° C.
233	40	Recovery	99%
241	50	Residue	1
252	60	Loss	Nil

Crude Spirit.

Specific Gravity at 60° F.	0·7700
Total Sulphur	0·381%
Initial Boiling Point	54·5° C.
Final Boiling Point	176° C.

Distillation Range (I.P.T.).

Temperature.		Temperature.	%
I.B.P.	38° C.	110	55·0
50° C.	3·0%	120	64·5
60	6·5	130	73·0
70	13·0	140	80·0
75	17·0	150	86·5
80	23·5	160	91·0
90	33·5	170	94·5
100	45·0	End point	180° C.
		%	97·5%

Carless-Coalene Refined Coal Spirit.

Specific Gravity at 60° F.	0·7625

Distillation Range.

Temperature.		Temperature.	
I.B.P.	44° C.	Up to 120° C.	77·0%
Up to 40° C.	—	130	87·0
50	—	140	93·0
60	2·0%	150	96·5
70	8·0	153·5	97·0
80	21·0	Residue	1·0
90	36·0	Loss	2·0
100	51·0	F.B.P.	153·5° C.
110	65·0		

Octane Number (Research Method).

C.F.R. Engine, 600 R.P.M.	86 to 92

The final boiling point can, of course, be put anywhere between 130° C. and 200° C. according to the purpose for which the spirit is required.

TAR AS A FUEL.*

By J. G. King, Ph.D., B.Sc., A.R.T.C., F.I.C., and
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Synopsis.

Tars and tar distillates require very little treatment to render them suitable for external combustion.

After a normal refining treatment gas spirits and low-boiling tar oils make excellent motor spirits, of high octane number, either for direct use or for blending purposes.

The burning of light creosote oil in spark-ignition internal-combustion engines, after giving some promising results, has proved on the whole to be a failure.

The slow-speed diesel engine requires very little adaptation to make it suitable for the combustion of heavy tar oils, but these cannot be used in the high-speed diesel engine, owing to the difficulty of obtaining rapid ignition. Suitable means have been found for the reduction of the ignition temperature and the ignition delay of tar oils, but none of these has yet proved a commercial proposition.

The present tendency is to regard tar less as a fuel and more as a raw material for the production of fuels by processes such as cracking and hydrogenation. The cracking process has a possible application to low-temperature tar or its distillates, but not to high-temperature tar or its distillates. The hydrogenation process gives large yields of motor spirit from all tars, but has not yet been successful in producing oil suitable for the high-speed diesel engine.

The amounts of tar produced during 1934 were 226 million gallons from gas undertakings, 136 million gallons from coke-oven plants and 4·7 million gallons from low-temperature carbonization plants. For the most part these tars are absorbed by the normal markets, which are more profitable than the fuel market. The road-tar market, for example, takes as much as 170 million gallons. The fuel market, therefore, can only hope to obtain the tar which may become surplus to normal requirements. Since our national requirements of fuel-oils alone amount to about 800 million gallons annually, it is evident that progress in the utilization of tar as a fuel has been retarded by the small and variable amounts available and the inevitable fluctuation of markets. This does not, of course, apply to tar products such as benzole, for which the normal market is that of fuel.

During the war and in the years immediately following, the potentialities of tar as a fuel were examined fairly thoroughly and the position was defined. Although a considerable amount of work has been done since then, that position has changed very little. It is not proposed, therefore, to detail in this paper the work which has been done, but rather to give a brief view of the present position regarding the use of coal tar and its distillates as fuels.

"Topped" Tar.

Owing to their content of ash, free carbon and pitch, and to their high ignition temperatures, tars, and especially high-temperature tars, are unsuitable for use as fuel for diesel engines. On the other hand, coal

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tars from all sources may be used for external combustion, although slight alterations to the burners and the air–fuel mixture ratio may be necessary. The tars must be reasonably free from water and such solid matter as can be readily removed by filtration; they must also be of suitable flash-point. The motor-spirit fraction is naturally removed from the tar before the latter is used as a boiler fuel; if the flash-point of the "topped" tar is then low owing to the presence of a small amount of low-boiling material produced during distillation, this may be removed by blowing air through the fuel.

The gross calorific values of tars vary from 16,500 to 17,000 B.Th.U. per lb. as compared with 19,000 B.Th.U. for petroleum oils. On a weight basis the calorific value of tar thus compares unfavourably with that of petroleum, but owing to the much higher specific gravity of tar there is little difference between the heating value of the two oils on a volume basis.

Although some tars may give trouble owing to their high viscosity, tars, generally, suffer from only one serious disadvantage: they contain a large proportion (20–60 per cent.) of high-boiling, resinous material, which may be thrown down as pitch if the tar is mixed with fuels of petroleum origin. It follows that tar cannot be used in admixture with petroleum fuel-oil or even alternated with it in the same installation.

Tar Distillates.

The distillation of tar is carried out in order to produce pitch, road tar and improved oils suitable for a variety of purposes. So long as there is a market for the first two materials it is unlikely that any appreciable quantity of "topped" tar will normally be available for use as boiler fuel. The surplus products from tar which are available for use as fuel-oils are thus mainly tar distillates, and these, therefore, merit more detailed consideration.

Boiler Fuel.—All tar distillates of appropriate boiling-range and flash-point can be used for external combustion without any special treatment. Certain low-temperature tar oils tend to form a waxy scum on storage, but this can be removed by the addition of a small proportion (usually less than 3 per cent.) of petroleum oil. Similarly naphthalene crystallizes from high-temperature tar distillates, and may require to be removed. In contrast to crude tars, tar distillates possess the great advantage of being completely miscible in all proportions with petroleum fuel-oils.

The calorific value of tar distillates is similar to that of "topped" tars, being rather low on a weight basis in comparison with that of commercial fuel-oils. This low calorific value is due, in part, to the tar acids, which are present in amounts varying from 10 to 40 per cent. The removal of tar acids from tar oils raises the calorific value by about 35 B.Th.U. for each one per cent. of tar acids removed.

Motor Spirit.—Motor spirits for use in automobiles or aeroplanes may be obtained from tars by distillation; they may also be obtained from the gas produced during the carbonization of coal by "stripping" with oil or a solid absorbent such as active carbon. The distribution of the spirit between the tar and the gas is variable, and is controlled by a number of factors which need not be considered here. There is therefore no essential

difference in character between the gas and the tar spirits, beyond the fact that the former contains a greater proportion of the more volatile constituents.

"Motor benzole" is produced mainly from the gas and tar from coke-oven and gasworks plants. The crude benzole consists largely of benzene and toluene, with smaller quantities of xylenes and unsaturated hydrocarbons. Up to very recent years it has been the common practice to remove practically the whole of the unsaturated hydrocarbons during the refining process with sulphuric acid; the losses entailed by this treatment amount to 10–20 per cent. This is obviously a wasteful process, and in order to reduce the amount of refining necessary, inhibitors (about 0·03 per cent.) are now widely used to prevent gum formation. Limited refining is still necessary to remove coloured and colour-forming bodies, sulphur, and compounds of objectionable odour; but the use of inhibitors makes it possible to retain a great proportion of the unsaturated hydrocarbons. The refining is chiefly necessary for the reduction of sulphur content, so that benzoles low in sulphur require little treatment, whereas the refining of benzoles rich in sulphur may still involve the removal of considerable quantities of unsaturated compounds. A great variety of compounds have been suggested for use as inhibitors for motor benzole, but the chief inhibitor actually employed has been cresol (mainly the *o*- and *p*- compounds), and it is understood that the combined use of catechol and cresol is beneficial, especially for more unstable spirits.

Motor benzole has a high anti-knock value, and on this account is generally employed as a blending fuel; its chief disadvantage is its high freezing point (—11° C.), which renders it unsuitable for use as an aviation fuel.

Owing mainly to revival of trade in the iron and steel industries and to the tax on imported spirit, the production of motor benzole has shown a continuous increase in recent years. Thus in the years 1932–1934 the annual production was 26, 31 and 40 million gallons.

The low-temperature carbonization of coal is potentially a source of valuable motor spirits; but the production at present is very small in relation to that of motor benzole. Low-temperature gas and tar spirits differ from motor benzole in containing unsaturated, aromatic and saturated hydrocarbons in roughly equal quantities. The gas spirit is the more volatile and, in general, the superior fuel, although it tends to give some little trouble in refining owing to its high content of unsaturated hydrocarbons; it resembles motor benzole in having a high octane number (87–90), and possesses the added advantage of having a much lower freezing point. It is understood that low-temperature gas spirit has been used exclusively by certain squadrons in the Royal Air Force with every success for the last few years.

The calorific values of the spirits obtained from coal compare favourably with those of petroleum spirits, as the following figures show :—

Calorific Value of Spirits (Gross).

	Low-Temp. Gas Spirit.	Low-Temp. Tar Spirit.	Motor Benzole.	Gasoline.
B.Th.U./lb. . . .	19,650	19,220	18,050	20,000
„ /pint . . .	18,720	19,540	19,800	18,450

Fuel-Oils for Use in Internal-Combustion Engines.—The tar distillate which has been available in the greatest quantity for use as a fuel is creosote. In common with other tar distillates, creosote has been produced in increasing quantity in the last few years, the total production in 1934 being 80 million gallons, as compared with 65 million in 1933 and 55 million in 1932. The market for creosote has been poor in recent years, but owing largely to the requirements of the coal hydrogenation plant of Imperial Chemical Industries, Ltd., there is, at present, a ready market for all surplus creosote.

As already stated, creosote can be readily used for external combustion, but it is too valuable a material to be used for this purpose, and a considerable amount of work has therefore been conducted with a view of making it suitable for use in the internal-combustion engine. The amount of heavy oil produced from low-temperature tar is only a small fraction of that produced by gasworks and coke-ovens, but it is slowly increasing; it is of importance inasmuch as its profitable disposal considerably affects the economics of the low-temperature carbonization process. Interest also attaches, therefore, to the possible use of low-temperature tar oils as diesel fuels.

The use of tar oils as fuels is naturally influenced very largely by the fiscal position with regard to oil fuel. The recently increased tax on petroleum diesel fuel will thus encourage the attempts to produce from tar heavy oils suitable for use in internal-combustion engines. Fuel-oils may consist of "light oils" or "heavy oils," "light oils" being defined by the Finance Act of 1928 as follows:—

"'Light oils' means hydrocarbon oils of which not less than 50 per cent. by volume distils at a temperature not exceeding 185° C. or of which not less than 95 per cent. by volume distils at a temperature not exceeding 240° C., or which give off an inflammable vapour at a temperature of less than 22·8° C., when tested in the manner prescribed by the Acts relating to petroleum."

Owing to the differential rates existing between 1933 and 1935 for vehicles propelled by heavy oils, there was an advantage in attempting to produce fuels of the "light oils" class from tar; but this advantage no longer exists, as the differential tax was abolished in 1935. However, the incentive to use tar oils of any kind in motor vehicles still remains, but there would not seem to be any great prospect of fuels produced from coal becoming widely used in the stationary or marine type of diesel engine unless all petroleum diesel fuel is taxed equally.

Tar oils differ from petroleum oils in possessing a much lower H/C ratio; thus the H/C ratios of creosote, low-temperature tar oil and crude petroleum are 0·8, 1·2 and 1·7, respectively. In other words, tar oils are aromatic, and petroleum oils generally paraffinic, in character. By virtue of this property tars yield excellent motor spirit of high anti-knock quality, but poor diesel fuel of high ignition temperature and long ignition delay. Thus tar oils have a spontaneous ignition temperature of 450–500° C., whereas that of petroleum oil is about 250° C. Hence compression-ignition engines which have been developed for burning petroleum oils would hardly be expected to be well suited to the combustion of tar oils. Further consideration of these oils is best given in terms of the three types of engine available.

The Slow-Speed Diesel Engine.—Although the specific gravity of tar oil is high, there is no difficulty in making the oil satisfactory in all other ordinary properties of viscosity, freezing point, distillation range, setting point, and sulphur, ash and water content. Tar oils fail badly only in regard to ignition temperature and ignition delay. These properties are of less importance in diesel engines of the slow-running type, and the burning of tar oils in such engines has therefore met with considerable success. Even with engines of this type, however, difficulties may be encountered with starting, erratic running and detonation, owing to the poor ignition quality of tar oils; but these difficulties can be largely overcome by the introduction of pilot ignition systems, and of improved nozzles and flame plates to give finer atomization.

The High-Speed Diesel Engine.—Although a slight modification to the slow-speed diesel engine may overcome the difficulty of the high ignition temperature of the fuel, this property, together with the long ignition delay of tar oils, renders them completely unsuitable for use in the modern, high-speed engine of the diesel type. It is apparent, therefore, that tar oils must be modified to suit this engine, or alternatively the engine must be modified to suit the fuel before further progress can be made.

Various means have accordingly been suggested for the reduction of the ignition temperature and of the ignition delay of tar oils, and these include:

1. The addition of a substantial proportion of a standard fuel-oil. This expedient alone is not sufficient to render tar oils suitable for the modern high-speed engine, and in any case can have only a limited application.
2. The addition of a small quantity of "dope" such as alkyl nitrates and nitrites (especially ethyl nitrate), iron penta-carbonylate and organic compounds containing a halogen atom and a nitrate group on adjacent carbon atoms. This method has given very promising results, but has not yet been developed to commercial success on account of the expensive nature of the dopes required.
3. The use of a catalyst chamber in front of the combustion chamber. Amongst the catalysts suggested are thorium oxide, platinum or palladium supported on asbestos wool and vanadium pentoxide supported on silica gel.

Further developments along these and similar lines will be awaited with great interest.

Since the modern high-speed diesel engine was developed specifically for the combustion of petroleum oil, there is much to be said for the suggestion that the best way of utilizing creosote and other tar oils is to design an engine to suit the properties of these oils. Many alterations in the design of the engine have therefore been made; these have had as their chief objects the improved atomization of the fuel and an increase of the temperature of the fuel either within or prior to, the combustion chamber. Up to the present, however, alterations of this nature have not met with any great success.

The Spark-Ignition Engine.—During the last six or seven years great interest has been displayed in the use of light creosote oil in the spark-ignition internal-combustion engine, especially in the experimental running of omnibuses. Some or all of the tar acids are removed from the creosote,

and benzole, and/or solvent naphtha, is added to keep the naphthalene in solution at low temperatures; a small proportion of the tar acids may be retained for the same purpose. Alternatively, both the tar acids and the naphthalene may be entirely removed. Such tar-oil fuels have the advantages of lower cost and higher octane number as compared with petroleum fuels, but these advantages have apparently not been large enough to outweigh the disadvantages which are enumerated below :—

1. The difficulty of obtaining supplies of uniform quality.
2. The cost of preparation of the fuel, since straight distillates cannot be employed.
3. The complications due to the necessity for using gasoline for starting-up and when idling.
4. The greater extent of crank-case dilution which is due to the high final-boiling-point of the creosote.
5. The increased mechanical troubles, such as those due to sooting or gumming of the plugs.
6. The objectionable odour of the exhaust gases (which are, however, relatively free from carbon monoxide).

In the absence of a sufficiently cheap dope, it is concluded that the only satisfactory solution to the problem of burning tar oils in the internal-combustion engine would be the designing of a special engine for the purpose. It is doubtful, however, whether this would be justified owing to the relatively small quantities of tar oil now available.

Tar as a Raw Material.

Owing to the difficulties mentioned above, tars and tar oils are being regarded less as fuels and more as raw materials for the production of fuels by such processes as cracking and hydrogenation.

Cracking.—High-temperature tars undergo a severe cracking treatment in the course of their production, and consequently consist largely of refractory material which is unsuitable for further treatment in the normal cracking process. Low-temperature tars are subjected to much less severe cracking conditions during production, and thus form more promising raw materials. They may be treated in the liquid phase at temperatures and pressures of the order of 450° C. and 200 lb. per sq. in. respectively, to give a yield of some 25 per cent. of motor spirit. The unsuitability of low-temperature tar as a cracking stock lies in the fact that it has a low H/C ratio of 1·0, whereas that of petroleum is 1·7. Motor spirit can therefore be produced from the former only at the expense of a large proportion of the tar being converted to coke. It is felt, however, that the cracking of low-temperature tar affords some prospect of development, especially in view of the possibility of producing fuel-oils, and even lubricating oils, by the polymerization of the unsaturated gaseous hydrocarbons formed during the process.

Hydrogenation.—The term "hydrogenation" denotes the process by means of which the hydrogen to carbon ratio and the boiling range of an oil may be altered by treatment at elevated temperatures (*ca.* 450 to 500° C.), and in the presence of hydrogen under high pressures (*ca.* 200 atm.); the rate of reaction is very much accelerated if catalysts are employed. From

the H/C ratios given in Table I below it is apparent that fuels similar to petroleum products can only be made from tars by the addition of hydrogen. If any process is capable of producing diesel fuel and motor spirit from tar, it should, therefore, be the hydrogenation process.

TABLE I.

Hydrogen to Carbon Ratios of Various Materials.

	High-Temp. Tar.	Creosote.	Low-Temp. Tar	Low-Temp. Tar Oil.	Petroleum Diesel Fuel.	Gasoline.
Carbon (C), per cent.	91·0	87·0	82·0	82·0	86·0	85·7
Disposable hydrogen (H), per cent. .	5·4	6·7	6·9	7·9	12·2	14·3
H/C atomic ratio .	0·71	0·92	1·01	1·17	1·7	2·0

Low-temperature tar is more amenable to hydrogenation than high-temperature tar, and tar distillates than crude tars; the presence of condensed nuclear compounds of high molecular weight renders the latter more difficult of treatment. Thus tar oils of the appropriate boiling range (*i.e.* not boiling above 300–325° C.) may be treated directly in the vapour phase at a temperature of about 500° C. Certain low-temperature tars may also be treated in this way, but most tars must be subjected to a preliminary treatment at a lower temperature (*ca.* 450° C.) in the liquid phase in order to hydrogenate the more refractory high-boiling materials. Low-temperature tar can be treated to yield an equal volume of motor spirit, and a large proportion of high-temperature tar, including a substantial part of the pitch, can similarly be converted to oil or motor spirit.

The conditions employed for hydrogenation depend upon the nature of the products desired. In the manufacture of motor spirit, for example, the conditions may be so regulated that the addition of hydrogen is kept at a minimum, and the spirit produced is therefore mainly aromatic in character and hence of high anti-knock value. On the other hand, for the production of diesel oil, the conditions may be so chosen as to favour the addition of hydrogen; the product is then similar in H/C ratio and spontaneous ignition temperature to a petroleum diesel oil. It is therefore possible that oil for the high-speed diesel engine may be made from tar by hydrogenation, although this has not yet been accomplished.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Seventieth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, London, on Monday, April 6th, 1936. In the absence of the President the Chair was occupied by Lieut.-Colonel S. J. M. Auld.

THE CHAIRMAN, in opening the meeting, said that Sir John Cadman much regretted that he was unable to preside, owing to his absence abroad. Personally, he felt honoured at having been asked to deputise for Sir John on the present occasion.

Much had been written and spoken about coal as a source of liquid fuel, but petroleum technologists and, he thought, the Institution as a whole, had had little opportunity of hearing authoritatively what the technical position really was. It was therefore with considerable pleasure he welcomed, both personally and on behalf of the Members, the three gentlemen who were to read papers on the present occasion. It was a privilege to obtain first-hand information from such distinguished authorities on the subject. None of them needed a personal introduction to the meeting. Dr. Lessing had been so long and intimately connected with coal that to chemists, at any rate, the word "coal" and the name "Lessing" were almost synonymous. Colonel Bristow more than any other man, he thought, had broken new ground in his own industry, and deserved the encomiums of all his countrymen for the work that he had done. Dr. King, the Chief Chemist of His Majesty's Fuel Research Station, and Mr. Crawley, one of his assistants, represented the detached view and the authority which could always be ascribed to the work of that magnificent institution.

The following papers were then presented for discussion :—

"Coal as a Source of Liquid Fuel." By R. LESSING, Ph.D., F.I.C., M.I.Chem.E.*

"Liquid Fuel from Coal obtained by Low-Temperature Carbonization." By Colonel W. A. BRISTOW, M.I.E.E., F.R.Ae.S.†

"Tar as a Fuel." By J. G. KING, Ph.D., B.Sc., A.R.T.C., F.I.C., and C. M. CAWLEY, Ph.D., M.Sc., A.R.C.S., D.I.C.‡

DISCUSSION.

THE CHAIRMAN, in proposing a very hearty vote of thanks to the authors of the three papers that had been read, said the papers had been most serviceable and instructive. He had come to the meeting with a number of questions and also a few doubts in his mind, but they had been to a great extent answered and dissipated.

The motion was carried by acclamation.

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* See pp. 577–582. † See pp. 583–594. ‡ See pp. 595–601.

THE CHAIRMAN, in opening the discussion, said he had always been particularly interested in the carbonization side of the utilization of coal. The clarification of the position by the authors that evening had proved of considerable value to him, and must be so, he was sure, to most of those present who gained their livelihood from petroleum and wanted to know what the position was with regard to the carbonization end of the formation of liquid fuels from coal and the possibility of their utilization. All three authors had stressed the point that the quantities involved were not large; they did not claim that the use of them would in any way revolutionize the fuel position. Nevertheless, they were important, and personally he wondered whether the coal tars, regarded generically, had had everything done for them that could be done in order to make them available as fuels for modern engines. He was not quite clear on that point even now. In the past the petroleum industry had over and over again altered its gasoline fuel to meet the engine design; but it was now quite definitely beginning to call a halt and looking to the engineers to take their turn by developing the engine to fit the fuel. Despite the remarks that had been made that evening, by Dr. King in particular, he wondered whether engineers should not be called upon to make the engine fit the fuel, rather than continually turn to the hydrocarbon industries to make the fuel conform to the engine. Was it not possible, if this attitude were adopted now by the coal industry, that collective engineering research on its behalf might result in the production of something in the way of a diesel engine that would answer the purpose? The Petroleum Industry has been more than ordinarily lucky that with the development of the high-speed diesel engine its products had proved outstandingly suitable as fuels. The high-speed diesel appeared to be so much the engine of the near future that the technical world would be justified in seeking reassurance that other fuels had not been merely submerged in the mighty flood of petroleum.

There was another point which he wished to raise in connection with cracking, with a view to fuel production for the internal-explosion engine. Colonel Bristow, when speaking of the motor spirit formed by fractionation of low-temperature tars, did not refer, as Dr. King had done, to the possibility of increasing the yields by cracking. That was a matter on which process research definitely appeared to have fallen short. One could not always depend on individual firms such as Colonel Bristow's, large as it was, to do that kind of work. The use of cracking to increase the quantity of motor spirit available from low-temperature tars was of special importance to-day, when not only were processes of straight cracking available, but there was also the possibility of thermal re-forming and polymerization of gases with the production of that "bit extra" which incidentally would have a particularly high octane rating. The gasoline engine was going to be with us for a long time yet. The luxury of hydrogenation might be torn from consideration at any time by a possibly ungrateful country, and he thought the two lines he suggested had not been sufficiently attended to.

MR. J. G. WITHERS said the question of the utilization of coal-oil distillates in heavy-oil engines seemed to have attracted a considerable amount of attention, but the results appeared to be somewhat dis-

appointing. If it could be argued that it was the duty of the engineer to re-design his engine to operate satisfactorily on fuel from coal, it would seem quite possible, and even probable, that the finished product would run still more successfully on petroleum products.

The addition of dopes to fuel oil introduced some difficulties from the practical point of view. He thought that all the dopes which had been tried up to the present must evaporate in the engine cylinders before they were effective, which meant that high-compression engines and engines with low-temperature cylinder walls would be less suited to those particular dopes. Engines with hot surfaces and lower compression ratios would run more satisfactorily on doped fuels. Colonel Bristow had referred to tests on an A.E.C. Comet engine, which, although a high-compression engine, had very hot surfaces inside the combustion chamber. An engine like the Gardner engine, with a much cooler combustion chamber, required a larger percentage of the dope to give the same reduction in ignition lag. In practice, sufficient of the dope would need to be added to the fuel to satisfy the coolest-running engines on the market. The most effective way of reducing the ignition lag seemed to be to introduce the dope into the air intake, but the quantities involved were so small that the metering mechanisms introduced practical difficulties. Another difficulty in regard to the use of dopes was that some of them corroded the working parts of the fuel injection system. Short test runs were unreliable, as insufficient time was given for the corrosion to take place. To test a doped fuel a run of at least 1000 miles would be necessary. The addition of dopes to the fuel oil generally reduced slightly the calorific value, in which case the fuel consumption was increased. Colonel Bristow had found that the rate of fuel consumption was higher when running on coal oil than on petroleum oil, but the difference was larger than could be accounted for by the fall in the calorific value.

Colonel Bristow, interposing, said the tests did not show that the fuel consumption was increased.

Mr. Withers said he thought Colonel Bristow had mentioned that the engine ran 9½ miles per gallon of coal oil and 11½ miles per gallon of petroleum oil.

There was also an indication that the quantity of dope added in the test referred to by Colonel Bristow was insufficient to reduce the delay time to the same value as that obtained with the mineral oil, as was indicated by the fact that one of the drivers commented on heavier combustion shock.

Mr. P. C. Pope said he thought Dr. Dunstan could give some information with regard to the effect of cracking on low-temperature oils, *e.g.* the increased amount of light spirit and the coke produced by the process.

Mr. J. Roberts said he had been very much interested in the three instructive papers which had been read that evening.

He had been very much impressed, in the first place, by Colonel Bristow's plain, unvarnished statement of what was being done at his works. Colonel Bristow had made it quite clear that those engaged in low-temperature carbonization must rely for the bulk of their revenue on the solid fuel, the liquid fuel side of it being relatively unimportant, especially from a financial

standpoint. That was what all the firms that were really producing the goods found; the only people who claimed anything else were those who failed to deliver the goods.

He was also interested in the success that had attended the efforts of Colonel Bristow's firm in dealing with the liquid fuel side of their business. Their solid fuel was so popular that it needed no words from him; the spirit was also establishing itself, and the fuel oil and the diesel oil seemed to be very promising. He felt that Colonel Bristow's company should be congratulated on the valuable pioneer work which they were doing.

The information given by Dr. Lessing in his paper was nearly all accurate and fundamental. He began by saying that in general those engaged in low-temperature carbonization had not paid sufficient attention to the coal itself, the raw material. That was true. It was only when people had really attacked the coal and tried to make the coal respond to treatment, instead of making the retorts in which the coal was treated respond to the coal, that real success had been achieved. There was a danger, however, in talking too much about the constitution of coal. For the last twenty years coal chemists had been harping on the constitution of coal, but, in spite of the enormous amount of research work which had been carried out, they had as yet provided no real information as to the constitution of coal, and it was not advisable for those who wished to attack the carbonizing business to wait until the coal chemists had elucidated the constitution of coal. Those chemists had said that coal could be divided into alpha, beta and gamma compounds, but those terms were just labels; they meant nothing. Dr. Marie Stopes said that coal could be divided into four components: vitrain, clarain, durain and fusain. Those were merely new names for old constituents, and at least three of them were just new labels. Dr. Stopes had now come forward with a number of other labels for other constituents of coal, and other people had devoted a great deal of time to the classification of coals.

As an illustration of the little value that such things possessed, he might say that about two or three years ago Colonel Bristow and he were at a Committee meeting at which low-temperature carbonization problems were being considered. There was a grandiose scheme on the table, and at that table there was a chemist who was renowned for his work on the classification of coals. A question arose as to a coal that was available for treatment, and that chemist wanted to know something about it. He did not ask anything at all about the alpha, beta or gamma compounds; he did not ask how much clarain, vitrain, fusain or durain the coal contained; he did not ask whether it belonged to the *para*-bituminous class, the *ortho–para*-bituminous class, or anything of that sort; he did not even want to know the carbon–hydrogen content. All he wanted to know was what was the volatile content of that coal. Similarly, he himself was quite sure that if Dr. Lessing had been at that table, all he would have asked was what was the ash content of the coal!

Mr. G. Stewart Taitt said he spoke as a layman with regard to the technical chemical matters under discussion; he lived abroad a great deal, and was rather out of touch with them. He thought, however, that he represented a considerable number of members of the Institution in putting to the authors of the papers a question of a very general nature

with regard to economics. He remembered that some years ago, when he was in this country, the question of low-temperature carbonization was brought before the general public, amongst other things, as ushering in an era of smokeless fuel all over the country. From the remarks made by Colonel Bristow and the other authors, he gathered that a successful low-temperature carbonization industry seemed to be based on using all the by-products as well as the liquid fuel, and that it had begun quite successfully, although many people doubted in the earlier years whether it would do so. If real success had attended it, was it too much to hope that almost all the coal supplies of the country would eventually be used in that way—to contribute to the liquid fuels used within the Empire, of which there was at present a lack, and to usher in the happy era of smokeless fuels for all towns? He would like to ask Colonel Bristow in particular whether such an era might be expected.

Mr. O. Thornycroft said he had been concerned with engines rather than with their fuels. He felt that the Chairman's remarks constituted a challenge to engineers to justify their position and to show that they had done something to make use of the recent improvement in fuels.

He could point to the advantage taken of improvements in the anti-knock quality of gasoline. During the last three years the C.F.R. octane number of aviation gasoline had been increased from about 73 to 87. This had enabled designers to increase the power of a given-sized engine by no less than 30 per cent. He had quoted aircraft engine performances because in aircraft engineering most advantage had been taken of fuel improvements.

With regard to the compression-ignition engine the art was much less advanced. Nevertheless progress was being made, and in this branch it was mainly in the development of engines which were less fuel sensitive. The point reached so far in this development was illustrated by the fact that small engines could now be designed to work satisfactorily with fuel having a cetene number as low as 30–35. The use of fuels having lower ignition quality than this would, he thought, present great difficulties.

In the papers and the discussion reference had been made to the use of "dopes" which in small concentrations would increase the ignitability of fuels for compression-ignition engines. It had been said that different types of engine responded in a greater or less degree to fuel improvement by "doping." This was a fact full of interest to the engine designer.

Having listened to the very interesting papers that had been read, he had to admit that he was still a little at sea as to whether or not tar distillates could be regarded as satisfactory fuels for internal-combustion engines. He was greatly interested in Colonel Bristow's remarkable results, but he would like to know whether the fuel, particularly the gasoline, was not objectionable from the point of view of gum formation. The anti-knock quality of such a fuel, given by Dr. King as 87–90 octane number, was very good indeed; but on the question of gum stability he still felt a little doubtful. His doubts had been strengthened rather than allayed while listening to Dr. King, who felt, apparently, that tar oils were better used as materials for hydrogenation than as fuels in their original state. On the other hand, it was impressive evidence that gasoline distilled from low-temperature tar had been accepted by the Air Ministry as a satisfactory fuel.

He would like to ask what was the ignition quality, expressed as cetene number, of the "doped" fuel used in the tests of the oil-engine rail-car referred to by Col. Bristow.

Mr. C. W. Wood said there were two questions which he would like to ask Dr. King. Dr. King had mentioned a figure of 0·6 million gallons. If that referred to low-temperature spirit, he would like to know whether it was the refined product, because, as far as he remembered, the Report of the Department of Mines for 1934 gave about 735,000 or 740,000 gallons as the output of low-temperature carbonization spirit. Did that difference represent the refining losses?

Secondly, would Dr. King explain a little more fully the interesting points he had made in connection with taxation?

Dr. A. E. Dunstan said that he had worked on the subject of the cracking of low-temperature tar oils many years ago, and there was really little to add to what had been said already. The obvious problem in cracking these materials was, of course, the adjustment of their particular hydrogen–carbon ratio. One started with a complex mixture in which the carbon–hydrogen ratio was very unfavourable to the production of light spirit, and the alteration of that ratio involved the production of a considerable amount of carbon. The subject was fully discussed at the International Bituminous Coal Conference at Pittsburgh in 1928.

He would like to emphasize the point that too much attention was given by coal-oil advocates to motor spirit. The diesel age was rapidly approaching, and it did appear to him rather remarkable that those interested in the coal side still paid so much attention to a material that necessarily contained a very high hydrogen content. (Incidentally he agreed with Mr. Withers, that to design a special engine to work on a particular fuel was not likely to appeal to the manufacturers.)

Whether or not a dope could be added to coal-oil diesel fuel remained to be ascertained in the future, but one would naturally imagine that the cost of a dope might make it prohibitive.

On the other hand, it seemed to him, speaking for the moment merely as a chemist, that on every ground, theoretical and practical, the carbon–hydrogen ratio must be rectified and balanced, and hydrogen must, of course, be introduced. Chemical compounds were required with the ratio of carbon to hydrogen that had been proved to be effective, and they could be obtained from tar oils, as Dr. King had pointed out, but again at a cost, and it seemed to him that ultimately the whole matter boiled down to the question of cost, unless, of course, economic nationalism brushed the question of cost on one side.

To-day the whole world had arrived at a remarkable and unique position of economic nationalism. Every nation was seeking by every possible means to put a ring fence round itself, in order to stop other nations sending in materials, and, when a nation did that, it inevitably stopped its own goods going out. He did not wish for a moment to pose as a politician; but it seemed to him an extraordinary thing, and one which to a man of science was almost incomprehensible, that a nation should deliberately add to the burden on its manufacturers when at the same time it also wanted to stop manufacturers in other countries sending their goods into its own country.

Mr. J. Romanes, in a written contribution, said: In his initial remarks on the coalification of vegetable matter Dr. Lessing rather gave the impression that he regarded peat, lignite, brown coal, bituminous coal and anthracite as successive stages in coalification, a process which he defined as a loss of oxygen, hydrogen and some carbon. If this is the case, then, on the average there must be a progressively higher ash content as one goes along the series from peat to anthracite. Is this so?

Is it not more generally accepted that in most cases the type of coal, within limits, was determined, at a very early stage of its history, by differences in raw material, conditions of deposition and processes of decomposition? Perhaps Dr. Lessing would say whether the ash percentages tend to bear out one or other of these theories.

Dr. J. G. King, in reply, said that Mr. Wood had questioned the discrepancy between the figure of 0·6 million gallons quoted for low-temperature spirit and the Mines Department figure for 1934 of 0·74 million gallons. Dr. King explained that the figure quoted by him was intended to represent approximately the production of refined spirit.

Mr. Wood had also asked for further amplification of the remarks made in connection with taxation. Dr. King, however, felt that this point was quite a small one, and was fully explained in the paper.

Dr. R. Lessing in his reply to the contribution by Mr. J. Romanes said: The fact that the ash content of commercial coals does not always appear to increase in conformity with the rise in rank is a problem which has presented difficulty to many students of coal formation in the past. In point of fact the explanation should be very simple. The bulk of the ash in coal as mined is derived from extraneous impurities, such as shale, pyrites and carbonate (ankerite) partings. The ash in the coal components proper is fairly typical, say 1–2 per cent. in vitrain and clarain, 6–7 per cent. (argillaceous) in ordinary durain and a mean of about 15 per cent. in fusain. If a coal deposit containing a preponderating proportion of vitrain and clarain is subjected to anthracitation, the ash in the anthracite will be low. Moreover, the conditions of high pressure which favour its formation tend to prevent the appearance of cracks which might be subsequently filled with deposits by infiltration of water (partings), and these are much less frequent in, say, Welsh anthracite, than in most banded coals of lower rank. There are, however, large deposits of anthracite, such as that in Pennsylvania, which have a relatively high ash content, and this must be ascribed to their raw material of lower rank having contained a higher proportion of durain.

CONTRIBUTION TO THE STUDY OF REFINING CRACKED DISTILLATES WITH HIGH SULPHUR CONTENT.*

By F. Sager, D.Sc. (Member).

Synopsis.

Treatment of cracked distillates with a given amount of sulphuric acid of a given concentration results in a definite sulphur content of the finished gasoline, if the reaction is carried to equilibrium conditions.

The equilibrium conditions for desulphurization of cracked distillates with a given amount of acid are reached in less than 60 seconds.

With the important proportions of acid necessary for reasonable desulphurization, contact periods, longer than strictly necessary for reaching equilibrium conditions, result in heavy losses of hydrocarbons. Those further losses of the less stable hydrocarbons mean increased gum stability.

Stopping the reaction when equilibrium conditions for desulphurization are reached means saving of valuable hydrocarbons. Additional stability can be obtained by adding a suitable gum inhibitor to the finished product (in the cases discussed in this paper, a natural inhibitor).

In respect to desulphurization, gum stability and polymerization losses, the true counter current, two-stage refining has a similar effect to single-stage refining, with a somewhat increased amount of acid.

Desulphurization of cracked distillates is one of the most difficult problems in petroleum refining. Considerable research work has been carried out in the past, and is still being carried out, with the aim of improving the economic results of sulphuric acid treatment, and of replacing sulphuric acid by some other refining agent.

Morrell and Egloff have studied the desulphurization of cracked distillates by sulphuric acid treatment.[1] The following of their conclusions are cited here for the sake of interest in regard to this paper :

" The degree of desulphurization increases with increase in concentration of acid and with increase of quantity of acid used. The degree of desulphurization to be obtained depends to a great extent on the character of the sulphur compounds present in the cracked distillate (or fraction thereof) to be treated.

" Increase in concentration of acid increases polymerization and solution losses.

" Reduction of solution loss is appreciable with reduction in temperature, but is substantially less than the decrease in polymerization."

To inhibit the heavy losses of hydrocarbons when desulphurizing cracked gasolines by sulphuric acid, Halloran [2] suggests cooling the cracked distillate to — 7° C., or still lower temperatures, before contacting with sulphuric acid. He states that, at those temperatures, strong sulphuric acid retains its activity as a solvent for sulphur compounds, but is less active as a polymerizing agent. Minus 7° C. is considered as the optimum temperature. At that temperature the acid is still sufficiently fluid to allow proper contacting with the cracked distillate. The low-temperature treatment,

* Paper received March 13th, 1936.

it is claimed by Halloran, gives a finished product with lower values for copper dish gum than treatment at higher temperatures. There are no published data for gum stability as determined by any of the oxygen-bomb tests now in use.

In this paper desulphurization by sulphuric acid treatment at atmospheric temperatures will be analysed from the kinetic side, with particular regard to polymerization loss and gum stability. A report of investigations on the influence of the time factor in acid refining of cracked distillates of low sulphur content has already been given in this Journal,[3] and no further mention will here be made of certain facts which were found to be valid for all cracked distillates (drop of octane number, formation of neutral esters, etc., as a function of the contact time).

The following examples will be studied in this paper :

(1) Iraq cracked distillate.
(2) Iranian cracked distillate.
(3) Venezuelan cracked distillate.

I. Iraq Cracked Distillate.

Characteristics of raw cracked distillate :—

Type of cracking plant	Dubbs
Specific Gravity	0·732
A.S.T.M. dist. I.B.P.	27° C.
100° C.	35 per cent.
F.B.P.	197° C.
Sulphur (lamp method)	0·34 per cent.

Refining conditions : 2 per cent. by weight acid (96 per cent. H_2SO_4), in one portion, mixing time equal to total contact time, varied from 4 to 124

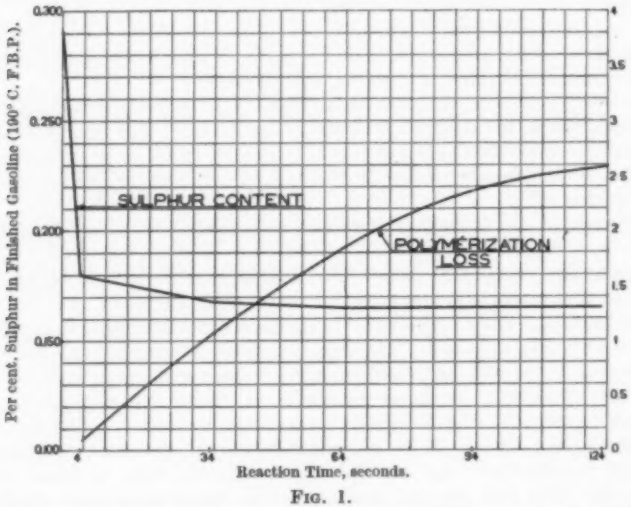

Fig. 1.

Treatment of Iraq cracked distillate with 2% by weight of 96% H_2SO_4.

seconds, centrifugal separation after given mixing time. Initial temperature 10° C., final reaction temperature, maximum for 124 seconds, 22° C.

The acid-treated distillate was neutralized with caustic soda solution, and redistilled in a Hempel apparatus until 175° C. were reached at the top of the column.

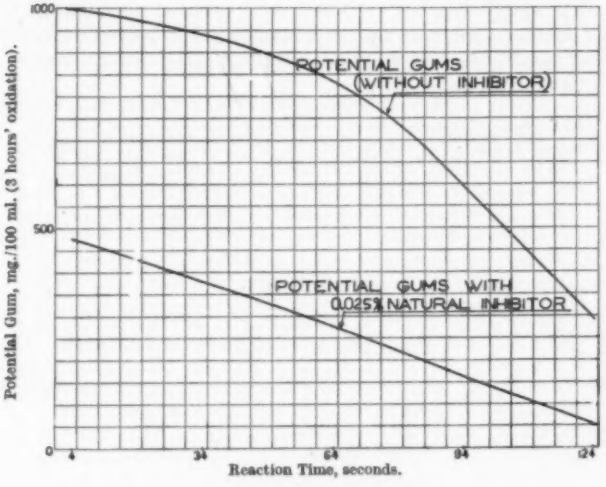

FIG. 2.

TREATMENT OF IRAQ CRACKED DISTILLATE WITH 2% BY WEIGHT OF 96% H_2SO_4.

The distillate obtained was doctor-treated. In Table I polymerization losses and qualities of the finished products as obtained with the various

TABLE I.

Effect of Contact Time on Acid Refining of Iraq Cracked Distillate, with 2 per cent. by Weight of 96 per cent. H_2SO_4.

Contact Time (seconds)	4	34	64	94	124
Polymerization loss (per cent.)	0·08	1·05	1·84	2·36	2·58
Qualities finished gasoline :					
Sulphur (per cent.)	0·180	0·168	0·165	0·165	0·165
Colour, Lovibond	plus 1	min. 1	min. 1	min. 1	min. 1
Actual gums (cold air jet) (mg./100 ml.)	2	less than 1			
Potential gums (Voorhees-Eisinger, 3 hours' oxidation (mg./100 ml.)	1000	940	830	590	300
Ditto, after addition of 0·025 per cent. by weight natural inhibitor	480	380	275	160	55

contact times are given. The polymerization loss was calculated by using the following formula :

$$A - \frac{B(C)}{100}$$

where A is per-cent. over at 175° C., including vapour loss, for the raw product, B is 100 minus solution loss, C is per-cent. over at 175° C., including vapour loss, for the acid-treated product.

As far as colour and actual gums are concerned, the product after 34 seconds' contacting can be considered to be as good as that after 124 seconds' contacting. After 34 seconds the equilibrium for sulphur removal is also very nearly reached. Values for potential gum decrease with increasing contact time, and are proportional to the polymerization losses, or, in other words, proportional to the elimination or transformation of the less stable hydrocarbons.

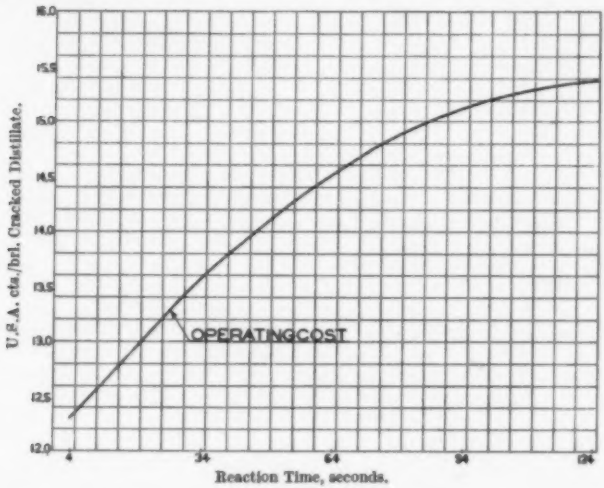

FIG. 3.
TREATMENT OF IRAQ CRACKED DISTILLATE WITH 2% BY WEIGHT OF 96% H_2SO_4.

In Table I it is also shown that, by addition of 0·025 per cent. by weight of natural inhibitor, the gum stability can be considerably increased. The products obtained after 34 and 64 seconds' contact time are thus rendered equal in gum stability to that obtained after 124 seconds' contact time. The natural inhibitor is isolated from the caustic soda solution, used for pre-treatment of the raw cracked distillate, by a stream of carbon dioxide gas, until the mother solution reaches a pH of 9. The question of the natural inhibitor has already been discussed in detail in this Journal.[4]

Figures for the influence of various amounts of acid on the refining results of Iraq cracked gasoline have been given by Egloff and Nelson.[5]

Table II shows the economical significance of the chemical data given in Table I. Total operating cost (including amortization, chemicals, losses, etc.), as a function of the reaction time is given for a medium-size plant (4 to 5000 brl./day), consisting of one-stage acid treatment, with means for instantaneous (centrifugal) separation of acid sludge after the desired contact time, and gravity-settling equipment for water and caustic-soda wash.

TABLE II.

Effect of Contact Time on the Cost of Acid Refining of Iraq Cracked Distillate with 2 per cent. by Weight of 96 per cent. H_2SO_4.

Contact time (seconds) . . .	4	34	64	94	124
Operating cost U.S.A. cts. per brl. of raw distillate . . .	12.30	13·58	14·52	15·14	15·38

II. IRANIAN CRACKED DISTILLATE.

Characteristics of raw cracked distillate :—

Type of cracking plant	Cross.
Specific Gravity	0·744
A.S.T.M. dist. I.B.P.	32° C.
100° C.	30 per cent.
F.B.P.	208° C.
Sulphur (lamp method)	0·165 per cent.

Refining conditions: 2 per cent. by weight of 96 per cent. H_2SO_4, in one portion, mixing time equal to total contact time, varied from 10 to 124 seconds, centrifugal separation after given contact time. Initial temperature 4° C., final reaction temperature, max. after 124 seconds, 10° C.

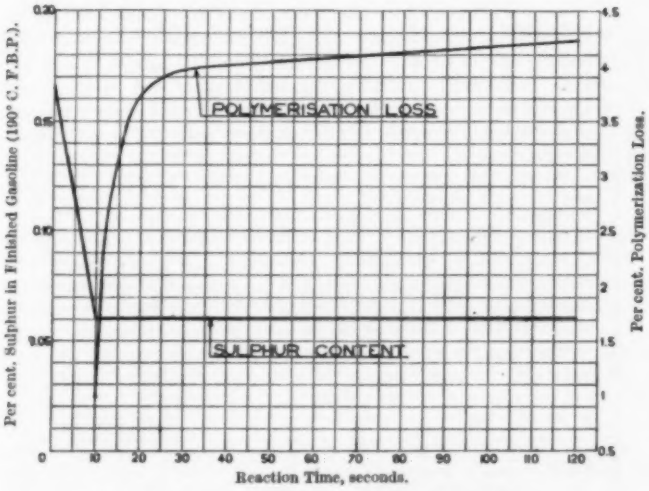

FIG. 4.

TREATMENT OF IRANIAN CRACKED DISTILLATE WITH 2% BY WEIGHT OF 96% H_2SO_4.

The acid-treated distillate was neutralized with caustic soda solution and redistilled in a Hempel apparatus until 190° C. were reached at the top of the column. The distillate obtained was doctor-treated.

In Table III polymerization losses and qualities of the finished product, as obtained with the various contact periods, are given.

TABLE III.

Effect of Contact Time on Acid Refining of Iranian Cracked Distillate with 2 per cent. by Weight of 96 per cent. H_2SO_4.

Contact time (seconds)	10	20	90	120
Polymerization loss (per cent.)	0·98	3·74	4·15	4·24
Qualities finished gasoline:				
Sulphur (per cent.)	0·061	0·061	0·061	0·061
Colour, Lovibond		plus 1, minus 1		
Actual gums, cold air jet (mg./100 ml.)		less than 1 mgr.		
Potential gums (Voorhees Eisinger, 5 hours' oxidation (mg./100 ml.)	80	32	8	4
Ditto, after addition of 0·025 per cent. by weight natural inhibitor	4	4	4	4

For this example it can be concluded that the equilibrium conditions for desulphurization are reached in 10 seconds.

The addition of 0·025 per cent. by weight of the natural inhibitor, present in the untreated sample, renders the product of any contact period above 10 seconds equal in gum stability to the product obtained by 120 seconds' contacting.

The following figures show the efficiency of sulphuric acid (96 per cent. H_2SO_4) for partial desulphurization of Iranian cracked distillate :—

1·0	per cent. by weight	0·095	per cent. sulphur in finished gasoline.
1·25	" "	0·085	" " " "
1·50	" "	0·075	" " " "

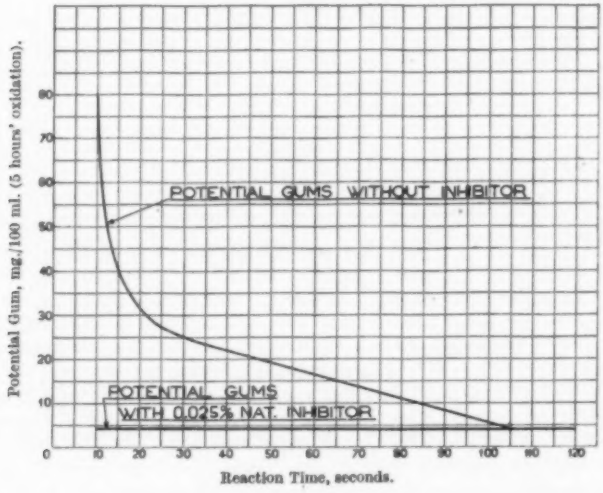

FIG. 5.

TREATMENT OF IRANIAN CRACKED DISTILLATE WITH 2% BY WEIGHT OF 96% H_2SO_4.

III. Venezuelan Cracked Distillate.

Characteristics of raw cracked distillate :

Type of cracking plant	Dubbs.
Specific Gravity	0·765
A.S.T.M. dist. I.B.P.	48° C.
100° C.	19 per cent.
F.B.P.	212° C.
Sulphur content (lamp method)	0·42 per cent.

Treatment with 1·8 per cent. by weight of 98 per cent. H_2SO_4, in one portion, at an initial temperature of 30° C., neutralization with caustic soda solution, redistillation in a Hempel apparatus, until 190° C. are reached at the top of the column, gives a gasoline, which, after caustic soda or doctor wash, contains 0·22 per cent. sulphur, if the refining action of the sulphuric acid has been allowed to proceed to equilibrium conditions for desulphurization. This equilibrium is reached in less than 60 seconds. The relationship between desulphurization, gum stability, and polymerization loss is very much similar to the case of Iraq cracked distillate.

Addition of natural inhibitor to Venezuelan cracked distillates has a similar effect on gum stability as experienced with Iraq products.

Morrell and Egloff have given results for the desulphurization of Venezuelan cracked distillate with different proportion of acid, with particular regard to the influence of the concentration of the acid.[1]

Up to now, only single acid treatment has been considered in this paper, and no attention has been directed to the quality of the waste acid and its potential value for further desulphurization. For each of the refining examples discussed in this paper the fresh waste acid had an acid value corresponding to 55 to 60 per cent. H_2SO_4 (titration with phenolphthalein).

Coming back to the above given example with Venezuelan cracked distillate, the use of the waste acid for pre-treatment, in true counter current, starting from 1·8 per cent. by weight of 98 per cent. H_2SO_4, gives a finished product (after redistillation, doctor or soda wash) with 0·16 per cent. sulphur content. The equilibrium conditions in the first (waste acid) stage are also reached in less than 60 seconds. The waste acid has a further polymerizing action on the hydrocarbons, and consequently causes additional gum stability of the final gasoline.

The acid, twice contacted with the cracked distillate, has an acid value corresponding to approximately 30 per cent. H_2SO_4. Its potential value for further desulphurization is practically nil.

Table IV.

Effect of Counter Current Acid Refining Venezuelan Cracked Distillate with 1·8 per cent. by Weight of 98 per cent. H_2SO_4.

Single stage	0·22 per cent. sulphur in finished gasoline.
Two stages	0·16 " " " "
Three stages	0·16 " " " "

References.

1 Morrell and Egloff, *Proc. World Petr. Cong.*, 1933, **2**, 13.
2 Halloran, *ibid.*, 1933, **2**, 3.
3 Sager, *J.I.P.T.*, 1934, **20**, 138.
4 Sager, *Ibid.*, 1934, **20**, 1044.
5 Egloff and Nelson, *Nat. Petr. News*, 19.1.35.

I.—ANALYTICAL FRACTIONATION OF HYDROCARBON GASES.*

By Wallace A. McMillan.

Synopsis.

Results of five years' work on the testing and proof of the absolute accuracy of methods and apparatus for the analytical fractionation of hydrocarbon gases by the use of synthetic gas mixture of known composition is presented. From the data and discussion included, it is apparent that reproducible results accurate to 0·1 per cent. can be attained only through rigid standardization of apparatus and methods. A complete discussion of dead space errors, column packings, heaters, condenser sections and thermocouples, together with the operating effects of reflux ratios, rates, sample sizes and methods of calculations, is given, and changes are outlined to obtain the accuracy and reproducibility required.

Methods for the quantitative separation of hydrocarbon gases into their individual constituents may be divided into two general classes, both of which depend on distillation at low temperatures and some degree of rectification. One relies entirely on extreme low pressures and low temperatures [5, 11, 15] to effect separation by multiple distillations with a minimum of rectification, using the wide differences in vapour pressures of the individual hydrocarbons below five millimetres absolute as the driving force. The other depends on an efficient rectifying column to obtain separations at low temperatures, but substantially atmospheric pressure.[1, 3, 4, 6, 16] Of the two, the rectification methods are used most, since fairly sharp separations are possible in only one operation, and the difficulties of high vacuum technique at low temperatures are not encountered. In addition, theoretical considerations show an obvious advantage of rectification over straight distillation even at low pressures.

As a result, present-day practice has discarded the tedious and cumbersome, although extremely accurate, Shepherd [11] type apparatus, and retained the basic features of the method for short-cut control work,[10] where accuracy is less essential than speed. At the same time, the Podbielniak and similar methods, in spite of the theoretical and practical advantages in their favour, have yielded erratic results and met with considerable criticism, primarily because analytical results could not be correlated when run on different apparatus or by different operators. Serious discrepancies are found too frequently when plant production or laboratory yields are checked against the analyses. Inasmuch as low-temperature rectification is both expensive and time-consuming, it was felt that it should be made to give accurate and reproducible results, or some other reasonably precise and less expensive method should be substituted. In the absence of definite proof as to the absolute accuracy of the method, it was in the same category as the Engler distillation, oil absorption, and pressure charcoal tests, which,

* Paper received April 1st, 1936.

while valuable for control work, are purely empirical, and therefore practically useless in exact engineering and the more involved technology of the petroleum industry.

After a careful study of the problem over a five-year period, during which hundreds of synthetic-gas mixtures were distilled under carefully controlled and observed conditions, it was concluded that low-temperature rectification of hydrocarbon gases can be made to give accurate reproducible results, but rigid standardization of both apparatus and technique is necessary. Podbielniak [7] reached much the same conclusion after a theoretical consideration of the problem supplemented by indirect tests, and the California Natural Gasoline Association [1] has standardized on the basis of reproducibility after a series of comparative tests on natural gases and gasolines. In neither case, however, was their apparatus or method checked against hydrocarbon mixtures of exactly known composition.

The present work has depended entirely on the distillation of synthetic mixtures of pure hydrocarbons of accurately known purity and composition under carefully controlled conditions; investigating as many characteristics of the columns as possible, from the boiling in the kettle to condensation in the reflux chamber, changing conditions, and even column construction and design, until the desired accuracy was obtained. The result has been the development of a column giving reproducible results of a known accuracy of 0·1 per cent. or better when run under standardized conditions. It is hoped that this work will provide a practical basis for the rigid standardization of apparatus and method proved necessary if extreme accuracy and reproducibility are desired.

Experimental.

The general method of attack consisted of purifying hydrocarbon gases, from ethane to butane, by combined chemical treatment and prolonged fractional distillation. These purified gases were stored in glass receivers, and their purities were checked by boiling point and by testing the vapour pressures of the initial and final ends of the fractions by a Shepherd [11, 12] differential manometer. In some cases other tests were also made, but it was felt that if the gas on fractionation showed a true and constant boiling point and the initial and final fractions showed the same vapour pressure then the gas would be considered pure.[17]

The purified gases were blended in a carefully evacuated all-glass system by condensing out a portion with liquid air and measuring the pressure difference in the calibrated blenders. In all cases the same amount of gas was found on distillation as was originally blended, or the sample was discarded.

The blends of known composition were then transferred to the proving system and fractionated by one of the columns under test. By the use of suitable condensation bulbs and all-glass manifolds, any sample could be recycled either to the same or one of the other columns for test. Thus any one fixed sample could be successively distilled under the same or different conditions in any or all of the columns under test.

Samples representative of those encountered in practice and special types then were fractionated under carefully controlled conditions, usually investigating one section of the apparatus or one type of procedure at a

time; usually completing one section before passing to another and gradually increasing the accuracy by change of design or conditions where necessary.

Apparatus.

Preliminary—Preliminary work was undertaken (1930) using a Podbielniak "Regular" type column with a 71-cm. (28-inch) rectifying section, 4·5 mm. in diameter with a 12·7-cm. condenser. A standard manometer hook-up with one open and one closed barometric manometer was also used. The purifying, storage and blending systems were of all glass and similar to the final design.

This preliminary unit was discarded as soon as it was proved that the column and auxiliary apparatus design was faulty and could not be made to give reasonable accuracy, primarily because of excessive dead space errors, which will be discussed later.

Final Apparatus.—Following completion of the preliminary study, a permanent set-up was made, as shown in the accompanying figures. It consisted of three essential all-glass systems: purifying and storage, blending, and testing and recycling. These were isolated to perform their individual functions, but interconnected to form a complete unit.

The purifying and storage unit consisted essentially of two independent columns with 91-cm. (36-inch) rectifying sections, 3·8 mm. in diameter, 17·8-cm. condensers, and heavy wire packings in combination with individual Y-type manometers and other necessary accessories. These were in turn manifolded top and bottom to four vertical banks of five 20-litre receivers each, and one special 48-litre receiver for large impure cuts with suitable connections allowed for introducing gases. Each vertical bank was then connected through a large condensation bulb to one of the individual 1500-ml. blenders. Twelve-millimetre leads connected to the pump manifolds at several places to ensure rapid and thorough evacuation.

With this set-up, either one or both columns could be used at one time for purifying; and pumping and filling of blenders could be done without interrupting the distillation schedules.

The blending unit (Fig. 1) consisted of four carefully calibrated 1500-ml. receivers with individual Y-type manometers, condensation bulbs, and connections to the storage system; with connections to a common pumping manifold and transfer line to the testing unit.

For the major portion of the work, the testing unit (Fig. 2) consisted of one Podbielniak "Regular" column [1]; one Podbielniak precision type [2]; and one California Natural Gasoline Association column.[3] Each was equipped with a constant-level check-valve manometer [4] and individual rate control-cocks; and all were manifolded into a common distillation manifold [5] using the same receivers; one of 1572·5 ml.[7] and the other [8] of 419·0-ml. capacity. The larger one was used for most of the work, and the smaller one only for very small fractions.

Both were provided with suitable condensation bulbs as shown, and a common storage receiver [9] of 5500-ml. capacity. Each column was also manifolded to the introductory and recycling line,[10] which was connected to the individual kettles [11] through suitable stopcocks.

Dead spaces were reduced as much as practicable. All three columns

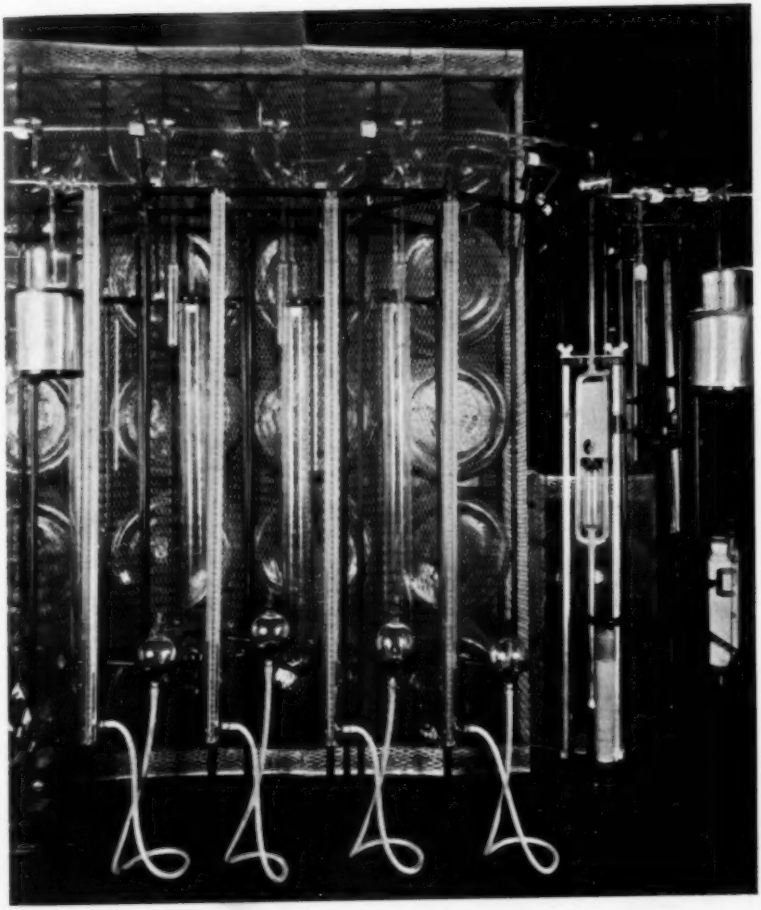

FIG. 1.
BLENDING UNIT

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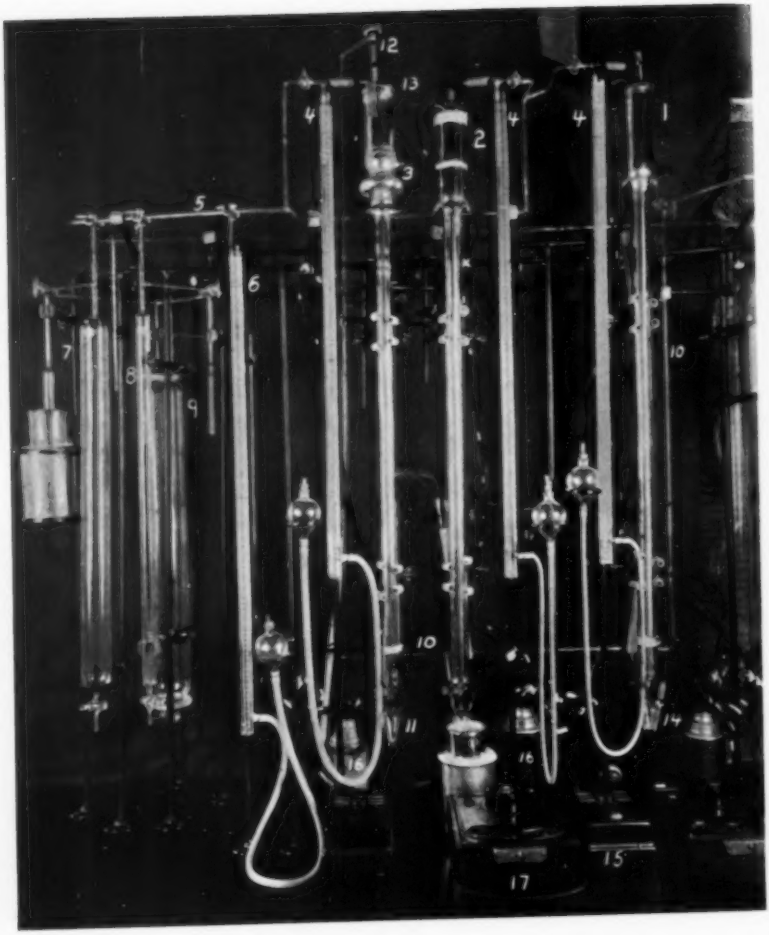

FIG. 2.
TESTING UNIT.

were built with 3·8-mm. distilling tubes 91·5 cm. (36 inches) long, with condensers 18·0 cm. in length, so as to be as comparable as possible. The columns shown were used for the greater portion of the work, but the precision type was later replaced by a Podbielniak " micro " column, and the regular type by a glass spiral column.

Reduced pressures were measured in the system by a double-range McLeod gauge protected by a liquid air-trap. Laboratory vacuum lines, a HyVac, a MegaVac and a General Electric Vacuum Pump backed by a MegaVac pump, were used alone and in combination to reach the extreme low pressures necessary to avoid contamination and ensure perfect transfer by condensation. The system was thoroughly outgassed before starting, and could be held at pressures of less than 0·5 micron for long periods.

All temperature measurements were made with copper–copper constantan thermocouples calibrated against the fixed temperature points of : boiling oxygen, freezing point of ethyl chloride, sublimation point of carbon dioxide, freezing point of mercury, melting point of water, and the boiling point of water. Smooth curves resulted, having maximum deviation at the ends, almost zero deviation along the centre, and agreeing well with the calculated values for this thermal junction.

Purification of Gases.

For the major portion of the work only four hydrocarbons (ethane, propane, *iso*butane and butane) were used. These were purified from commercial gases by combined chemical scrubbings and repeated fractional distillations as indicated.

Ethane.—The commercial gas was scrubbed through 30 per cent. fuming acid, 98 per cent. and 79 per cent. sulphuric acid, and 43 per cent. caustic, then passed through soda lime and anhydrone towers. The scrubbed gas was then distilled in the purifying columns, discarding all material boiling above or below the plateau. The overhead gas was re-scrubbed once by a train similar to the first and refractionated as many times as necessary, discarding heads and tails each time, until the vapour pressure of the first and last fraction was the same when compared in a Shepherd differential manometer. The boiling point of the purified material was 184·9° K. at 760 mm. absolute pressure.

Propane.—This gas was scrubbed through the same strength chemicals, and handled the same as for the ethane, except that more refractionations were necessary to reach the required purity. The boiling point of the material used in the blends was 230·8–230·9° K.

Iso*butane.*—Since the *iso*butane was the most impure of the commercial gases, it was dried and distilled once to eliminate as much contamination as possible, and then treated in 48-litre lots with pure liquid bromine, allowing the mixture to stand in diffused light for 24 hours and then neutralizing with an excess of caustic. The partly purified residual gas was subsequently treated the same as ethane except substituting 95 and 79 per cent. sulphuric for the stronger acids. After the preliminary treat with bromine, no further trace of olefins was encountered, and the final material after repeated fractionations boiled at 260·9° K.

Butane.—The normal butane was treated the same as ethane, except

substituting the same strength acids as for *iso*butane. The portion passing the Shepherd manometer test boiled at 273·5° K.

Some vapour-density determinations were made, and also absolute vapour pressures taken; but it was felt that if the material showed exactly the same boiling point for a number of successive fractionations, in which the end fractions were always discarded regardless of their boiling point, and the initial and final portion of the distillation showed the same vapour pressure, then the fraction should be pure.[17]

Procedure.

Synthesis of Mixtures of Known Composition.—For the preparation of synthetic mixtures and their transfer to the distillation unit, it was necessary to evacuate the complete blending system, the column to be tested, and the manifolds, condensers and receivers of the distillation unit to a pressure of 5·0 microns or less. The system was then shut in and allowed to stand, testing the pressure at intervals until it was certain that no leaks existed. If any leak developed, the system was tested by sections until it was isolated and eliminated.

The receivers were then cut out and the pressure further reduced. Usually, with the pumps in good order and using the liquid air trap, pressure was quickly reduced to 0·5 micron or less. When completely evacuated, the blenders were each filled with a pure gas from the storage unit, previously isolating the condensers from the manifold by closing the cocks. Pressures and temperatures of the gases were allowed to stabilize and carefully read and recorded.

Predetermined portions of each pure component were then drawn into their respective condensation bulbs by immersing them in liquid air and gradually opening the stopcocks. Pressures and temperatures were again read and recorded. The amount of gas drawn from each receiver was proportional to the pressure drop and, since the receiver volumes were known, the amount was readily calculated. Constant room temperature was maintained by a system of thermostats, and held constant for several hours before the samples were taken, since it was found that temperature adjustments in the gases were quite slow.

Blending and Transferring Mixtures.—While the portions of gas were being drawn, the receiving system was further pumped to a pressure of 0·5 micron or less. All cocks were then closed and the system was isolated except for the transfer line, the still on one column and the blending manifold. The Dewar pots surrounding the condensers were then lowered, and one of them was used to immerse the still in liquid air.

As the condensation bulbs warmed up, their contents were vaporized and passed into the still, where they were recondensed. In order to speed up this transfer, the condensation bulbs were heated by immersion in a beaker of cold water. Care was taken, however, not to heat the contents of the bulbs too rapidly, as explosive " bumping " then took place. When all the liquid disappeared, the bulbs were heated with a soft Bunsen or alcohol flame until all the frost disappeared and the condensers could be wiped dry.

When all active bubbling of the liquid air around the still due to con-

densation of the mixture ceased, the cock on the kettle was closed. The cocks on the manifold were also closed, the McLeod gauge read, and the residual pressure recorded.

During condensation and transfer of the mixture, the receivers were pumped further, until the pressure was 0·5 micron or less. They were then closed to the manifold and opened towards the receiver manometer by a 90° counter-clockwise turn. The mixture was now in the still; the column isolated from the manifolds; the receivers pumped and ready, and distillation could be started.

Distillation and Recycling.—No specific method of distillation can be given, since for this work various combinations of changes were used for each series of runs. In general, they followed standard practice.

Residues were determined by shutting in the column; reading the pressure in the receiver; then condensing all the material into the condensation bulb immersed in liquid air. A new initial reading was taken, and the distillation or pulling over of residues continued as before. Temperatures were maintained constant to 0·5° F. for the receivers and pressures read to 0·25 mm.

In order to recycle the gas for distillation on another column, or under different conditions, the column and manifolds were pumped as before; the transfer line blocked off from the blenders and opened to the receiver and column.

The still was then immersed in liquid air and the cock on the condensation bulb slowly opened. Material was condensed into the still until all bubbling of the liquid air had ceased, the residual pressure was checked, and the cocks on the still and condensation bulbs were again closed and distillation was made as before.

Data.

Dead Space Errors—During preliminary work it was found that three dead spaces existed, each of which decreased the efficiency of separation and made the results worthless for small samples. These led directly to the abandonment of the first set-up after only a small amount of work had been done.

Using a standard manometer arrangement, the first dead space consists of the volume from above the thermocouple junctions in the condenser to the receiving system. This is shown in Fig. 3, "old type," and includes the volume of the manifold to the rate-cock and the volume above the operating level in the column manometer. It was found in the first tests that as much as 31 ml. of gas would be lost in these connections and not detected in the distillation. This meant that as much as 2·0 per cent. of the lighter material in small sample distillations would be vaporized while building up pressure and, since it was beyond the thermocouples, it was not detected.

In the case of a gas sample, the first fraction is usually large, but in the case of a gasoline distillation the light ends are present in very small amount, and using such an arrangement they are not detected. This has led to frequent discrepancies when vapour pressures were calculated against the analysis, or vapour lock studies correlated with composition.

Several methods have been proposed for detecting these light ends. One suggested the use of air to fill the manometer before starting the distillation,[13] but was found to give widely erratic results. Use of a

preliminary Hempel distillation to concentrate the light ends has also been proposed, but such a procedure requires two distillations and losses in handling. The best solution to the problem at present is to reduce this dead space to as small a volume as possible. The " new arrangement,"

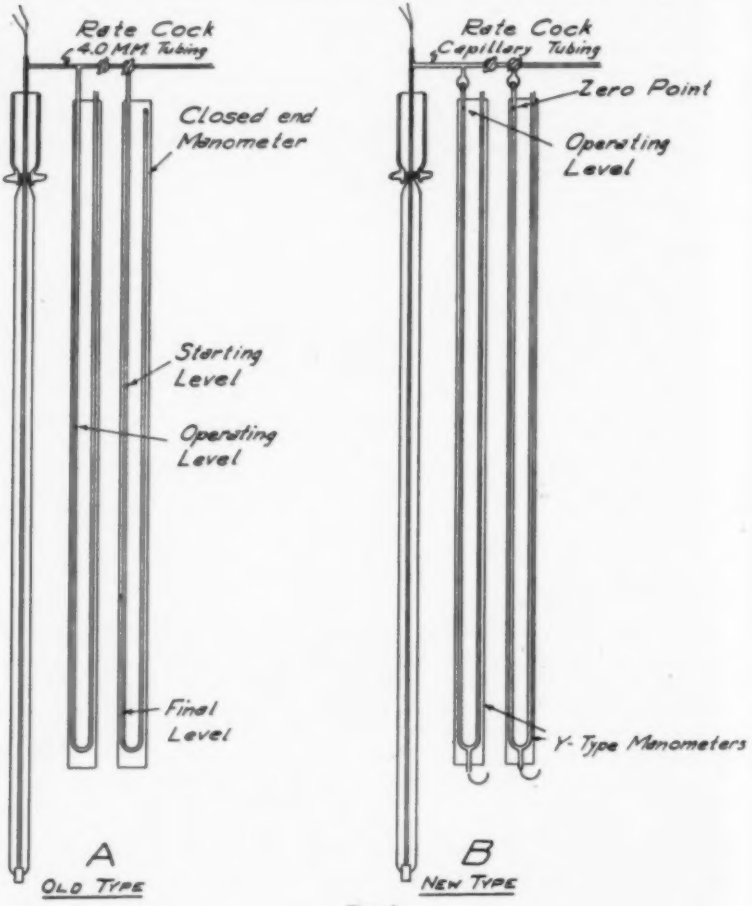

FIG. 3.

ELIMINATION OF DEAD SPACE.

shown in Fig. 3, substitutes a Y-type manometer for the conventional open-end manometer, and the operating level is raised to 2·0 cm. below the base of the check value. Using as short connections as possible and semi-capillary 2-mm. tubing to the rate-cock and top of the check-valve, this dead space has been reduced from 30 ml. to about 0·5 ml., including all volume above the thermocouple junctions. Such a decrease in volume also

resulted in much less lag between temperature and pressure measurements, with a consequent further increase in accuracy. This arrangement has since been adopted by the California Natural Gasoline Association.[2]

The receiver manometer has likewise been a source of error in the conventional set-up where a closed-end barometric manometer is used. This is likewise shown in Fig. 3. It can readily be seen that when using the closed-end manometer, the volume of the open leg increases as pressure builds up in the receiving system and, unless corrected, together with inequality of bore corrections, may cause a change of volume as large as 10·0 ml. Use of a Y-type manometer, where the mercury is always returned to a constant reference point before reading, has eliminated this error without adding to the difficulty of operation.

The third dead space was found at the end of gas distillations, and consisted of the volumes of the kettle, column and connections to the rate-cock on the manifold. It was found that at the ends of distillations, at a point where the packing was almost dry, a false break was always obtained, and the amount of gas left at this point was always a constant for any one column, regardless of the size of sample or its composition. It was also noted that the volume of the gas from the beginning of the false break to the end of the distillation was equal to the volume of the kettle, column and manifold connections to the rate-cock. This fact has been checked on the purification of ethane, propane, *iso*butane and butane; on synthetic two component ethane–propane and *iso*butane–butane mixtures; on four component mixtures; and on natural gases of different compositions.

The following proof is offered. During the distillation of ethane it was noted that as the material became more and more pure and the sample hence smaller and smaller, its calculated percentage by analysis became larger, until a certain maximum point was reached, at which point the calculated percentage by analysis started to become progressively smaller. Such a result would logically lead to the conclusion that there must be some source of contamination of the product. Accordingly, the entire apparatus was re-checked, but found to have absolutely no source of contamination. On calculating the results from " millimetres distilled " to " millilitres distilled," it was found that, following the maximum percentage point, the residues in each case were almost exactly the same, and approached as a minimum the value of 199·0 ml.

When the volume of the kettle, column, manometer and connections was calculated, the result was approximately 200·0 ml. Accordingly, there seemed to be a definite relationship between the two results. The run sheets were again inspected, and yielded the information that the temperature always rose when the wire packing became dry, and the volume left at this point was almost invariably 199·0 to 200·0 ml., or the dead-space volume for that particular column arrangement. It was also noted that, regardless of the size of sample (20 to 12 litres), the result was the same.

Exactly the same thing was found in the purification of propane, where the residues varied from 248·0 ml. towards a minimum of 200·0 ml., regardless of the size of sample, which has varied from 24·5 to 9·5 litres of vapour.

The assumption has been further verified by using a precision-type Podbielniak column on the analysis of a plant dry gas. Dry gas runs 204 and 205A by one operator and 204A and 205 by a different operator all gave

11·75 ± 0·75 mm. for the pentane plus residue, even though the sample volumes varied from 3500·0 to 4200·0 mm. (28·0 to 36·0 litres), and sample G-204 was a 0·8 GPM gas, whilst G-205 was of only 0·6 GPM.

The dead space calculated to about 186·0 ml. and the pentane plus residue to 87·0 ml. (minimum), but since the column was operating at 360·0 mm. absolute for the butane–*iso*butane separation, the dead space would be reduced to 360/760 × 186 = 88·0 ml.; hence within the error of the calculations the dead space was again equal to the volume of the residue. This, of course, does not mean that no *iso*pentane and heavier was present, but only proves that if the amount present is less than the volume of the dead space, then the amount obtained will be equal to the dead space, and the percentage, with a fixed volume of kettle, column, manometer and connections, will vary inversely as the size of the sample.

Hence in the customary procedure for dry gas analysis the material reported as pentanes plus is almost without exception subject to error as high as 100 per cent. of that fraction. That is, the analysis will, for ordinary columns, even though no *iso*pentane is actually present, show a pentane plus residue which will be approximately equal to the dead space volume.

When such a condition exists, it cannot be detected by the operator when handling the break exactly as for the other breaks during distillation. In such cases it is standard procedure, when the pressure drops and the millivoltmeter no longer gives a constant reading, but tends to fall, to shut in the column by the control cock on the manifold and at the same time add a little liquid air to the condensing bath. This reduces the pressure slightly (2 or 3 cm.) below distillation pressure. Pressure is again allowed to build up to distillation pressure; the millivoltmeter and receiver manometer readings are taken; a very small amount of gas is taken into the bottles; the column is again shut in, and the procedure repeated. There is no way for the operator to know that his condensing bath temperature is artificially warming up above the boiling point of component, even though he is adding small amounts of air. The false break so obtained is to all appearances a real break.

That something has been wrong, with dry gas fundamental analyses has been suspected for some time, since, in engineering and experimental work, invariably the hydrocarbon balances calculated from wet and dry gas analyses showed less than the amount of hydrocarbon actually recovered. This discrepancy was attributed to the uncertainty of the analysis, as regards the pentanes, due to the very small amounts present. However, even when enormous samples such as 650·0 ml. of liquid (usual sample 50 to 70 ml. liquid) were run the results were very little better. This, of course, was due to the extra dead space of the large kettle, which balanced out the additional accuracy gained by the large sample. Since that time the hypothesis has been that the large value for pentanes and heavier was due to absorption oil carried with the gas.

In order to check the previous conclusion, three series of runs were made on each of three columns under test, using the same samples in each case. The results are shown in Figs. 4, 5 and 6. In each case the dead space was a constant for each particular column, regardless of the amount of butane or the total volume of the sample. In order to make absolutely certain that the effect could not be due to a trace of heavier material in the butane

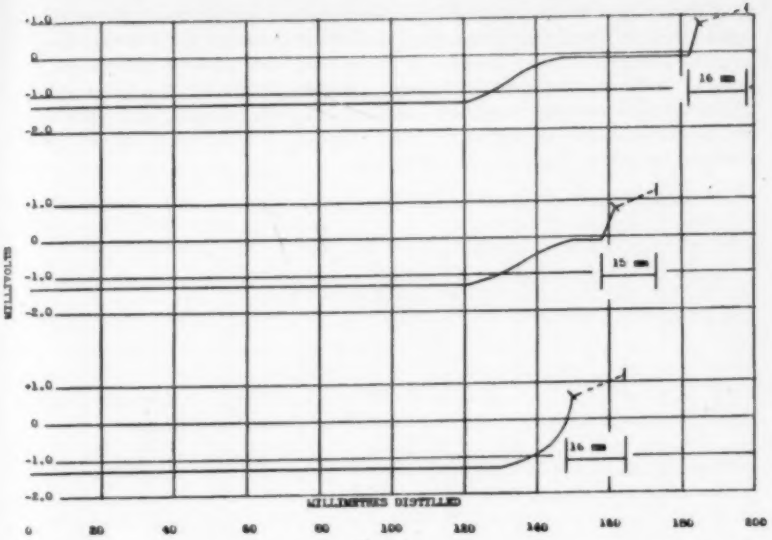

FIG. 4.

DEAD SPACE—COLUMN P1.

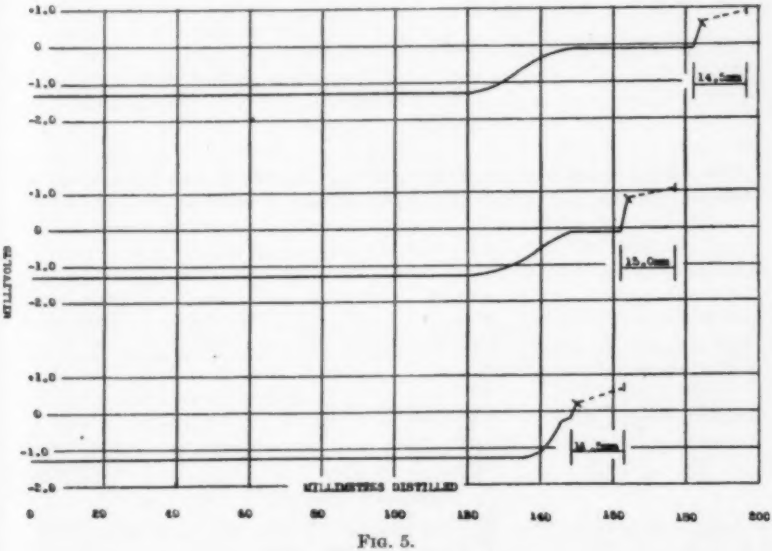

FIG. 5.

DEAD SPACE—COLUMN R1.

(which was almost an impossibility after the rigid purification), the samples were made up by adding successive portions of the same stock butane to the original sample. If any heavier material had been present, the successive series would have shown increasing volumes following the false break. However, the residue remained constant for each column, and calculated to the same volume as previously determined by calibration. Table I shows the results taken from the above figures.

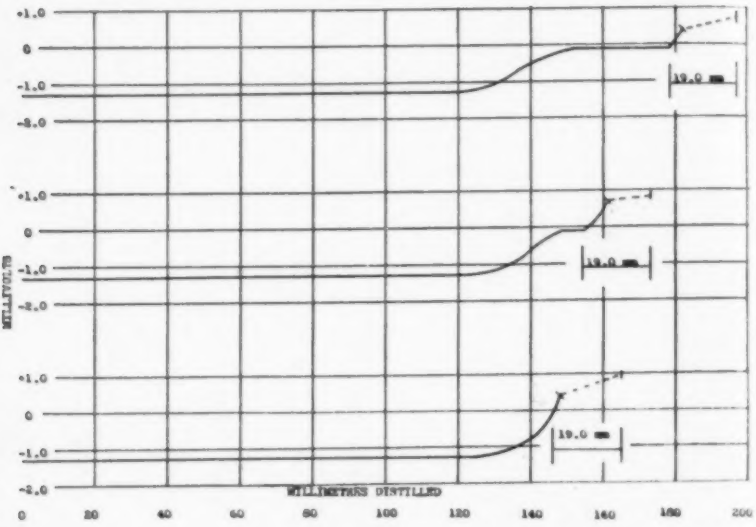

FIG. 6.

DEAD SPACE—COLUMN C2.

It will be noted that the dead space by calculation and the actual calibrated volumes are, within the limits of error, remarkably close.

TABLE I.

Run No.	Column.	Dead Space from Analysis mm.	Average for Column mm.	Average Converted to ml.	Actual Calibrated Vol. ml.
323	P1	16·0			
423	P1	15·0			
521	P1	16·0	15·7	64·5	65·4
321	R1	14·5			
422	R1	15·0			
522	R1	14·5	14·5	59·8	60·1
322	C2	19·0			
421	C2	19·0			
523	C2	19·0	19·0	78·0	79·7

There are four methods for reduction of the dead space so as to bring it within the limit of error of the determination. In the order of their desirability they are :—

1. Filling kettle with mercury.
2. Use of micro-column.
3. Reduction of pressure.
4. Use of a " chaser."

The most practicable method is to fill the kettle with mercury after it has become dry and before reducing pressure. It must, of course, be supported to prevent breakage. If the pressure is then reduced to 400·0 mm. absolute or below, the dead space becomes less than 5·0 millilitres or 1·0 mm. with a 3800-ml. receiver, which is about the limit of measurement of the method.

The use of an auxiliary or " micro-column " for the handling of small end fractions has been developed by Fitch.[4] When used, the residue remaining in the ordinary column is transferred to the micro-column at the end of the propane plateau by combined mercury and liquid air displacement. The smaller column has a very small-diameter fractionating section and a very small bulb, which cuts down the dead space, so that by simple reduction of pressure the error introduced by the end dead space is reduced below the error of measurement. The use of a micro-column has several serious disadvantages. The use of mercury in transferring residues is objectionable, as liquid or gaseous hydrocarbons may be trapped off in the mercury or along the walls of the connections, so that the accuracy is actually decreased. It likewise takes extra time to make the transfer and bring the second column to equilibrium. Also, in spite of the reduction in diameter of the fractionating section, there is a decrease in the length to diameter ratio with a consequent decrease in efficiency.

By using the smallest possible kettle (25 ml. or less) it is sometimes possible to bring the dead space within the limit of error by simply reducing the pressure to 150 or 50 mm. absolute. Simple calculation shows when this is possible.

The addition of a substance of higher boiling point than the heaviest component present has been suggested and tried as a means of eliminating dead space. The theory is that the substance added will gradually displace the heaviest component up the column, and when a sharp increase in temperature is indicated it means that all the hydrocarbon has been displaced and the distillation is at an end. The addition of methyl alcohol, toluol and other substances has been proposed. However, the substance added must not form constant-boiling mixtures with the hydrocarbons, and must be stable over the temperature range necessary. Likewise, the heaviest component must be known definitely. A few experiments using a purified mineral seal oil were very unsatisfactory.

The use of mercury and reduction of pressure is felt to be, for the present at least, the most simple and best solution for the elimination of dead space error.

Column Packings.

Even after eliminating all dead spaces possible and increasing the length of the columns, the first tests on *iso*butane–butane mixtures gave poor results. Binary mixtures containing as much as 6·5 per cent. *iso*butane in

butane could not be quantitatively separated on the C.N.G.A. or either of the Podbielniak columns under test. In fact, even its presence could not

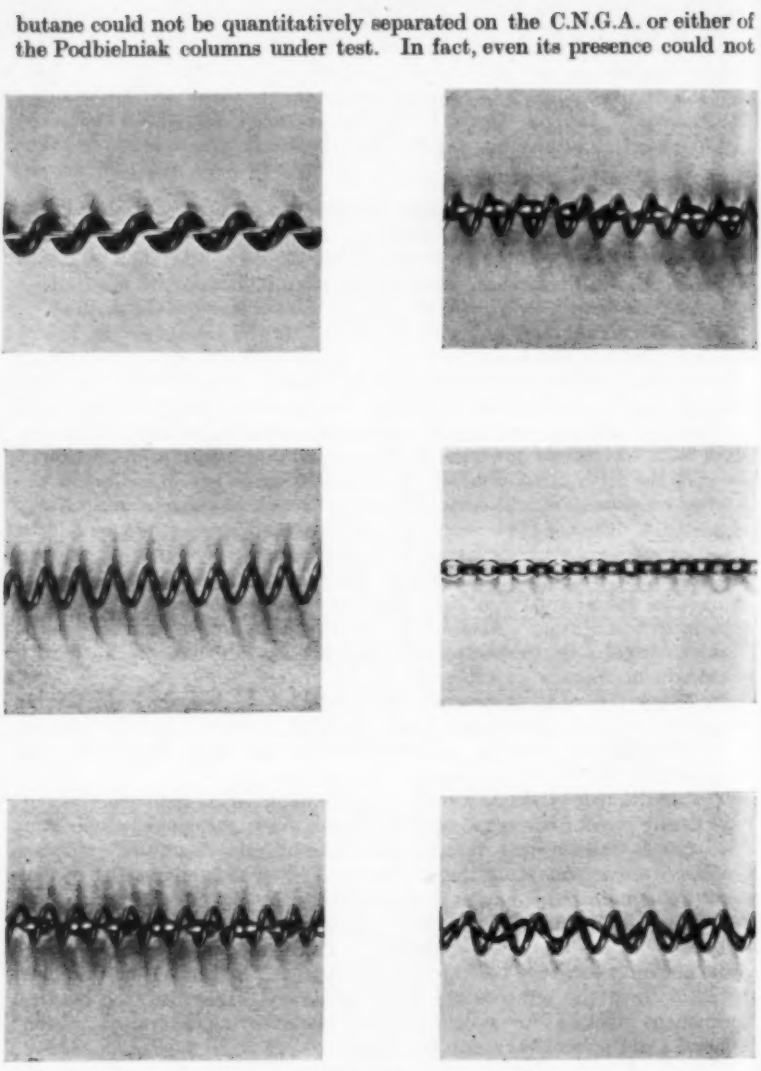

FIG. 7.
COLUMN PACKING.

be detected, since no *iso*butane plateau was obtained on distillation, and the only indication was a slight curvature at the beginning of the butane plateau.

At that time all three columns were using 8-turn-per-inch spirals of No. 22 B. & S. gauge wire. From previous observations it was suspected that channelling was taking place in the packing. The test was accordingly stopped, and a gas containing suspended fog particles was introduced at the bottom and liquid at the top. It was immediately noted that there were two currents of ascending vapours—one spiralling slowly up between the turns of the spiral, while the second, and by far the larger stream, was flowing linearly through the centre of the spiral and into the condenser. Obviously, this central stream was in contact with the reflux only at the outer edges and, since the vapour velocity was greater in the centre, a substantial portion of the flow was not being subjected to fractionation except in the condenser. This undoubtedly explains in some part why the use of a longer condenser has always improved the fractionation of this type of column. It means that the condenser, instead of merely supplying reflux, has actually been doing a portion of the rectification by partial condensation. The consequent poor efficiency was directly attributable to poor contacting of vapours and reflux.

As a further proof of the inefficiency of the single-wire packing, it was removed from the column and distillation of a 50–50 *iso*butane–butane mixture gave almost identical results as with it in. The only effect of this packing was to decrease the effective diameter and slightly increase the surface over which the reflux spread.

The C.N.G.A. standard packing of 8 turns per inch of No. 22 gauge wire with a $4\frac{1}{2}$-turn-per-inch inner spiral was only slightly better than the single spiral.

In all, eighteen different packing variations, some of which are shown in Fig. 7, were tried, from the standard 6-turn-per-inch No. 22 gauge single spiral to small silver-plated jeweller's chain, but it was not until the centre free space was entirely eliminated that good separations were obtained. A 6-turn-per-inch No. 16 gauge spiral with a No. 16 gauge straight wire central insert gave the best results in 3·8-mm. distilling tubes at low rates, but became inoperative due to flooding at high rates. A 6-turn-per-inch No. 16 gauge spiral with a 6-turn-per-inch longitudinal flat spiral insert of No. 29 B. & S. flat ribbon $\frac{1}{16}$ inch wide also gave good separations, and had higher capacity. However, the best packing for all types of service was found to be a 6-turn-per-inch No. 15 gauge brass spiral with a No. 23 gauge straight wire insert for non-corrosive samples or a $5\frac{1}{4}$-turn-per-inch No. 14 gauge aluminium spiral, filed to fit, with a No. 23 gauge nichrome insert.

Jeweller's chain packing gave poor results. Due to channelling and flooding, the chain was less efficient than any of the spiral packings, and added to the difficulty of operation.

In Fig. 8 are shown two curves, one with the old 8-turn-per-inch single spiral, and the other with a new 6-turn-per-inch No. 15 gauge spiral with a No. 23 gauge straight wire insert. The runs are on the same sample and under the same conditions except for the difference in packings. The improvement is all the more striking when it is realized that the curve shown is one of the best obtained with the old-type packing, and only an average curve with the new type.

The change of packings is noteworthy, inasmuch as it has raised the

recovery of *iso*butane from *iso*butane–butane mixtures from a maximum of slightly over 70 per cent. to a minimum of 90 per cent. In addition, there has also been a decided improvement in the reproducibility of results. For any one column the breaks, when plotted for a wide range of mixtures of the butanes, coincide almost exactly. Apparently, with any fixed packing, there is a characteristic break for each column, which is always obtained under optimum conditions of rectification, and is a measure of the rectification efficiency of that type of packing in that particular column.

It has been found that when using the new packing, abrupt changes in operation must be avoided. The packing works very efficiently and easily on practically all rates up to 200·0 or more millilitres per minute, but if the rate-cock is suddenly opened, or any other relatively violent change is

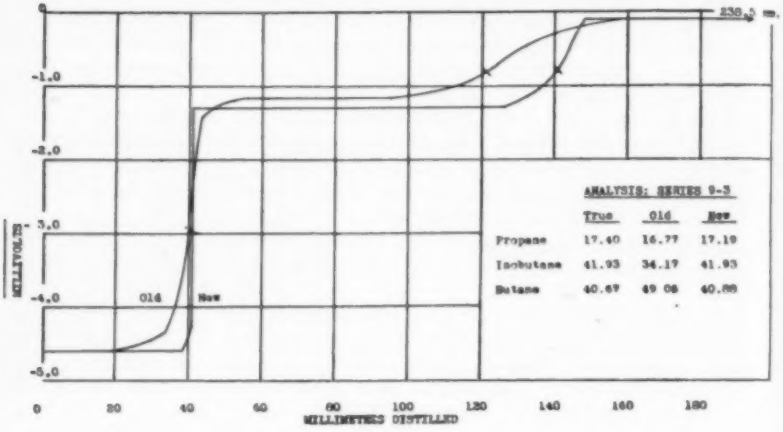

FIG. 8.

OLD VERSUS NEW PACKINGS.

made, the column will flood badly, in which case it takes considerable time to re-establish conditions. In the hands of experienced operators it is about as easy to operate as any single packing, and in any case is no more difficult to use than double packing.

As with previous type packings, it should fit the walls snugly and the central wire insert should be a force fit for best results.

HEAT INPUT CONTROL.

One of the most important factors involved in the separation of close-boiling constituents is the boiling in the still. It was found to be almost impossible to boil the last traces of *iso*butane out of an *iso*butane–butane mixture, and even the last traces of methane were removed only with vigorous boiling from a sample of ethane and heavier, although the difference in boiling point was more than 70° C.

Fig. 9 shows two curves which were run under identical conditions, except that one sample was boiled vigorously by an auxiliary heater, while the

other was weathered by the heat of the atmosphere. It is obvious that a much smoother and truer curve resulted from the controlled heat input.

Both internal and external heaters were used during the tests, and in practically all cases the results favoured the use of internal heaters—that is, electric heaters immersed directly in the liquefied gases. The reason for the better results is undoubtedly in the difference in the type of boiling with the two types of heaters. An external one usually gives rise to a small number of large bubbles in the liquid, and sometimes even to violent "bumping" due to local superheating and sudden evolution of vapours. The internal heater acts exactly opposite. It gives off large numbers of small bubbles, which gently but thoroughly agitate the liquid. In no case has serious bumping ever been observed. Four inches of No. 30 nichrome

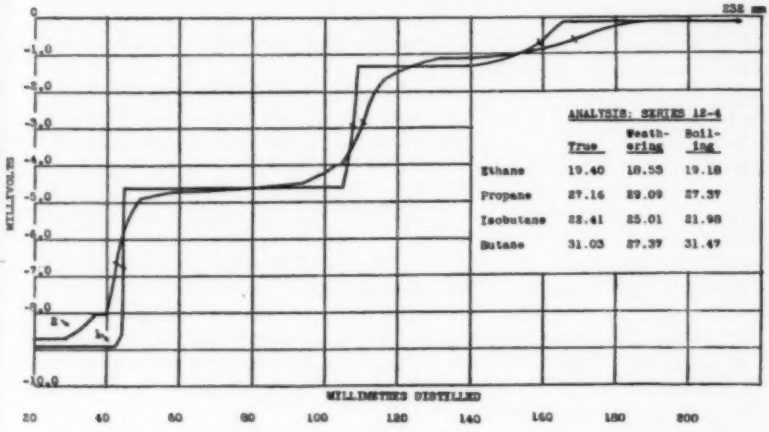

FIG. 9.

COMPARATIVE CURVES.

wire make a satisfactory heater for use in conjunction with a 1- to 6-volt adjustable transformer with an auxiliary 10-0-ohm rheostat in series for fine adjustment.

The use of external heaters is necessary when the kettle is filled with mercury at the end of the distillation, and most kettles should be fitted with both types. Tapering the lower end of the kettle tends to keep the heater immersed for a longer time and results in better agitation and boiling of the heavier fractions.

SUPERHEATING OF VAPOURS.

During one of the tests on packings a bad turn at the bottom of the spiral contacted the drip indicator and caused continuous flooding in the lower section of the column for about 15 cm. (6 inches). However, when the results were plotted at the end of the run, it was found that the flooding in the lower section had not lowered the fractionation efficiency, as would be expected from the decrease in effective length. The run was repeated

under slightly different conditions, but still flooding, with the same results on all the columns under test. In no case was the fractionation decreased anywhere in proportion to the decrease in effective length of the distilling tube.

The obvious solution was that the lower section was performing some work other than rectification. It is believed that this lower section, of at least 15 cm., merely removes superheat added between the surface of the liquid and the fractionating section, since that portion of the column is not jacketed and is exposed to a temperature considerably higher than the boiling points of the liquids being distilled.

A Dewar pot surrounding the kettle and extending to its top did not improve operation, except in so far as it eliminated temperature fluctuations due to draughts in the room. A cotton plug in the mouth of the Dewar flask improved conditions somewhat, but the addition of liquid air to it to cool the confined air to the temperature of the boiling liquid made the column almost unmanageable.

A double wrapping of one-eighth inch asbestos cord was then tried in addition to the dry Dewar flask and cotton plug. The results improved immediately. Part of this improvement is probably due, in the case of the precision and old-type columns, to the fact that at present the reflux, in dropping from the dripper, sometimes comes in contact with the walls of the connection and, previous to insulating this section, it was immediately re-vaporized and returned to the column, thus overloading it with the heavier constituent, with consequent loss of efficiency. With the insulation, once this section is cooled, the reflux is allowed to re-enter the kettle.

This difficulty is not encountered in the case of the C.N.G.A. column, since the kettle connection is shorter and much larger in diameter than in either of the other columns. It may be that the higher efficiency shown by the C.N.G.A. column is due to that fact, since all the rest of the dimensions are almost exactly the same.

No trouble has been encountered since the insulation was added, and the efficiency has increased from about 90 per cent. maximum to 97 to 99·5 per cent.

Effect of Reflux Ratio.

Probably no one factor has contributed more to the general non-reproducibility of results by different operators and different apparatus than reflux ratios. At present no definite reflux ratios are specified in any of the recognized procedure,[6, 1] so that the matter is left entirely in the hands of the operators, some of whom use light reflux and some heavy, as fits their individual preferences. The general tendency seems to be to use the heaviest reflux possible without flooding, since "infinite reflux"[8] is theoretically probably the best condition for perfect separation. For this type of operation, however, it is actually the worst condition for efficient operation.

Figs. 10, 11 and 12 show the effect of reflux ratios on three types of columns under test when run at approximately constant rate and using the same sample. All three show the same characteristics of peak efficiency at medium rather than at high or low reflux ratios; the C.N.G.A. being the most efficient, but peaking more sharply than the other columns.

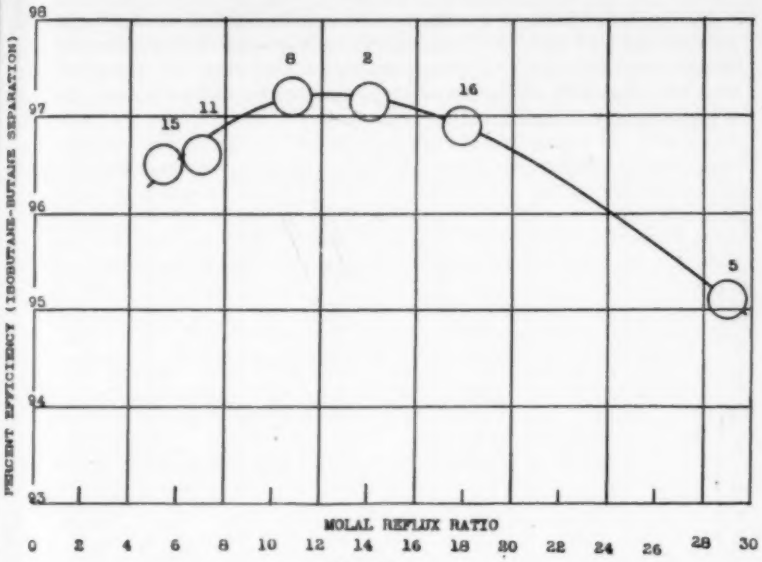

FIG. 10.

EFFECT OF REFLUX RATIO—COLUMN P1.

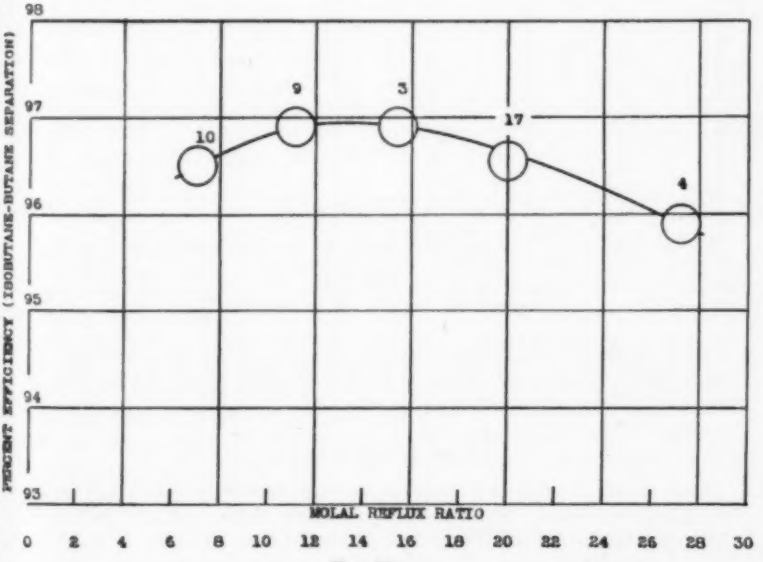

FIG. 11.

EFFECT OF REFLUX RATIO—COLUMN R1.

The reproducibility of results can be seen in Fig. 12, by comparing run 12 with 14, and 1 with 13. Both sets of check runs are well within the limits of experimental error. Similar curves, peaking over the same interval, were obtained with all the binary mixtures tested and for similar types of columns where tested.

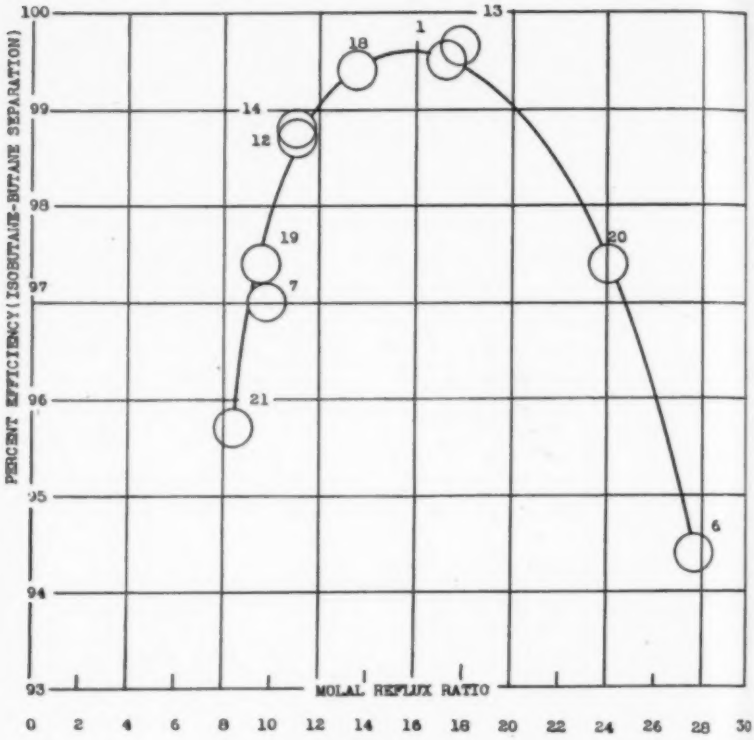

FIG. 12.

EFFECT OF REFLUX RATIO—COLUMN C2.

From these results, it seems that in order to maintain maximum efficiency, molal reflux ratios of 14 to 19 should be specified for the C.N.G.A. and 11 to 15 for the other type columns.

DISTILLATION RATES.

Rate of distillation is a most important factor in obtaining accurate reproducible results. At extremely low rates, using a 15 to 1 reflux ratio, the separations are invariably good, and quite reproducible. However, this leads to excessive time of distillation; hence a balance must be set up between results and time of analysis.

It was found that if the analysis was speeded up—within reason—on the plateaus and slowed down on the breaks to a rate of not over 10 millilitres of gas per minute, good rectification could be obtained and the accuracy maintained within the tolerance of 0·1 per cent. This, obviously, does not mean that an analysis can be run in three or four hours or less. Under the best conditions an ordinary refinery gas should take about six hours. Including introduction of sample, distillation and calculation of results, the total time averages about eight hours per sample. If run any faster, the results will be in error more than 0·1 per cent.

The rates given in Table II have been established as maximums but for best conditions should not be reached.

TABLE II.

Material.	Rate (ml. vapour per minute).
Air and hydrogen (during introduction)	25
Methane	150
Methane break	5–10
Ethylene (if appreciable)	25
Ethylene break	5
Ethane	100
Ethane break	5–10
Propylene–propane	100
Propane break	5–7
*Iso*butane–butylene	10
*Iso*butane break	5
N-Butane–butylenes	10
N-Butane break	5

In the case of plateaus, the above rates may be used, except for propylene–propane, only as long as the millivoltmeter is constant within 0·05 millivolt. If it falls off more than that, the column should be shut in, liquid air added and the rate reduced. Rates of greater than 10 millilitres per minute on the breaks gave poor results in all cases.

CONDENSER SECTION.

The most important, and at the same time by its very nature the most difficult, phase of this study has been the condenser section test. Its importance was never fully appreciated until actual changes were made in the condenser section and their effects noted on the subsequent distillation results. Until the development of the C.N.G.A. type column, it was too expensive a matter to experiment with the condenser, as each change required complete rebuilding. Consequently, virtually the only change in condenser section, since the original columns of Podbielniak, has been a gradual lengthening of the condenser tube, and even this change to improve accuracy was dictated only by the failure of the original packing to do its share of the work.

Even now, when the condenser section can be changed with a minimum of trouble, it was still a complicated and time-consuming problem, since it was not concerned with only one variable, but with a multitude of interdependent factors. The length, diameter, surface-volume relation, position

of thermocouples, temperature differential between condensing vapours and refrigerant, temperature gradient from top to bottom of condenser, type of heat transfer medium in the condenser bath, and overall heat transfer are all inter-related, and each one must be considered in its proper relationship.

The purpose of the test was twofold : to improve further the accuracy of separation, and to remove irregularities found in most distillation curves. The first object was, of course, paramount. The second is almost equally important now that the method has been extended to refinery and highly cracked gases.

It has been known, almost since the first Podbielniak columns were introduced, that a characteristic hump, or reverse break, is sometimes produced at the end of the methane, ethane and propane fractions just previous to the real break. That is, at the end of a plateau, the temperature starts to rise, then falls back almost to the plateau before starting a break. Such behaviour is common, but the resulting curve, as usually determined, is slurred by the operator taking only one or two readings at the beginning of a break, which results in a smoother rise to the vertical break line. In some cases the slur becomes so long as to actually resemble a small plateau, which, it is believed, has given rise to the reporting of such compounds as *cyclo*butane,[14] *cyclo*propane, and methylacetylene, when none is present, but the slur merely corresponds to their boiling points.

So long as only natural gases were being analysed, the irregularities exhibited by the curve were of only minor importance, provided good separation was obtained, since it was known that only paraffins were present. However, refinery and reformed natural gases contain, in addition to the paraffins : olefins, diolefins, acetylenes, cyclic compounds, and constant-boiling mixtures of their various combinations ; the boiling points and properties of which are little known. Since all of the later compounds, except the paraffins and some of the olefins, occur in only very limited amounts, it is necessary that the distillation curves be free from irregularities, so as to enable their detection and identification when present.

The absence of the known acetylene–ethane constant-boiling mixture in reported analyses and the rather frequent reporting of the rare gases methylacetylene and *cyclo*propane can almost undoubtedly be attributed to misinterpretation of the irregularities of the common distillation curve.

The phenomenon of reversed breaks was not observed in the case of *iso*butane–butane separations, where the break is normally slurred, but has been observed in practically all ethane–propane, methane–ethane and propane–*iso*butane breaks. In the preliminary work, with the original column, reverses were shown on almost all ethane–propane separations at atmospheric pressure. It was likewise found that the reverses could be practically eliminated by reducing operating pressures to 160 mm., absolute or lower, and that each successive decrease below atmospheric increased the sharpness of the break. This is shown in Fig. 13. It was further determined that the sharpness of the reverse was dependent on the reflux, since very high reflux rates gave sharp reverses with almost vertical breaks, and more nearly accurate results.

The new columns in the final apparatus set up exhibited the same reverses on both ethane–propane and propane–*iso*butane separations in spite

of the elimination of dead spaces, improved packing and better control of heat input. Hence the most logical and only offender was the condenser itself.

Preliminary work was done on eleven different sizes and types of condenser tubes, most of which were plain, but some contained varying sizes of wire packings, and one was made up of indented bulbs. It was found that improved efficiency was obtained with each reduction in effective condenser-tube volume, whether the reduction was made by reducing the tube size,

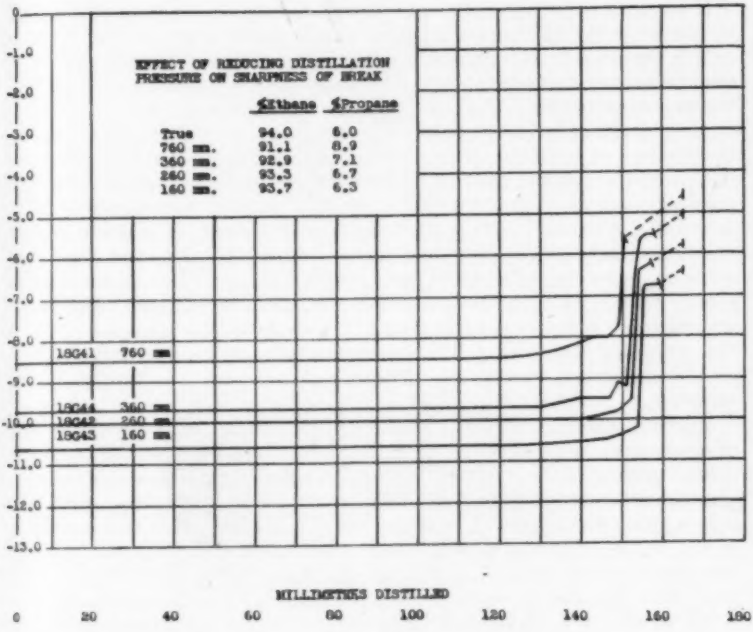

FIG. 13.

EFFECT OF REDUCING DISTILLATION PRESSURE.

adding packing or reducing pressure. This checked the conclusions of the preliminary work.

Both experiments gave sharper, cleaner breaks with small vapour volumes in the condenser, although the problem was approached from the different angles of reducing volume by pressure reduction, and reducing vapour volume by re-design of the condenser section. It was obvious that the best course was re-design, since it corrected, at least partly, the cause of the trouble. Further improvement, if necessary, could then be provided by pressure reduction.

Of the eleven preliminary sections tested, only two types were considered worth a further trial. One was a 3·25-mm. I.D. tube, and the other a

special, double concentric-tube condenser. Both were of small volume, and the latter had a large surface to volume ratio.

After a series of runs the double-tubed condenser was discarded, since it did not give consistent results under all conditions of operation, was quite fragile, and rather costly.

The final condenser adopted was a 3·35-mm. I.D. straight tube, indented at 6·5-mm. (¼-inch) intervals for the lower 5·5 cm. of its length. The indentations gave more surface, reduced volume and caused better mixing; thus giving slightly better results than the straight tube alone.

Decreasing the volume of the condenser likewise led to improved results by reducing the lag between temperature measurements at the thermocouple junctions and volume measurements at the manometers. It is obvious that the smaller the volume of gas between the temperature and volume measurements, the more accurate the results will be.

In conjunction with the test on the condenser tube, work was done on the method of applying refrigeration to it. It was found that the usual dry-packed condenser gave excessive time lag using one set of tubes and unsteady operation, and flooding using the other. Operation with both in series or in parallel was equally unsatisfactory, due to continuous adjustments necessary. Gasoline baths, as used in the C.N.G.A. and older type columns, gave erratic results when not stirred, and only slightly better results when agitated, as the speed of stirring had a pronounced effect on the separations. A better method than either of the others consisted of filling the condenser bath with ¼-inch aluminium balls with a distributor similar to the one shown in Fig. 14. The top of the bath was insulated with asbestos.

Means of applying refrigeration were varied almost as much as the type of condenser. Using the original light gasoline baths, it was found that the coldest portion of the condenser was at the bottom, thus reversing the temperature gradient necessary for best fractionation and providing reflux over only a short portion at the bottom of the condenser. This was corrected, partly by the substitution of the aluminium beads which widened the cold zone and provided more rapid heat interchange. In fact, results were quite good after the change, but still using the standard C.N.G.A. evaporator.

Better results were obtained, however, as soon as introducing liquid air direct on the top of the bath was tried. Air consumption was negligible, and the only difficulty was the extreme supersensitivity of the column. The addition of more than one drop of air at a time completely flooded the condenser, and put the column temporarily out of control. Cotton wadding and various types of distributors on top of the beads were also unsatisfactory until small holes were drilled in one of the distributors to allow part of the liquid air to drip on to the beads directly.

The final arrangement which gave the desired results was a 3·35-mm. I.D. condenser tube, indented for the lower 5·5 cm. at 6·0-mm. intervals to approximately three-eighths the diameter; surrounded by a fairly tight fitting close-wound spiral of No. 16 gauge bare copper wire. The condenser was filled with 250 ml. of ¼-inch aluminium beads with the evaporator (Fig. 14) setting on top, but with beads occupying the cutaway portion to a point even with the top of the body of the distributor. The whole was then covered with a loose-fitting piece of ⅛-inch asbestos paper, a ¼-inch

layer of long fibre shredded asbestos and then more loose-fitting circles of $\frac{1}{8}$-inch asbestos paper until even with the top of the bath. The insulation should not be too tight, as it must provide for the escape of the expanded

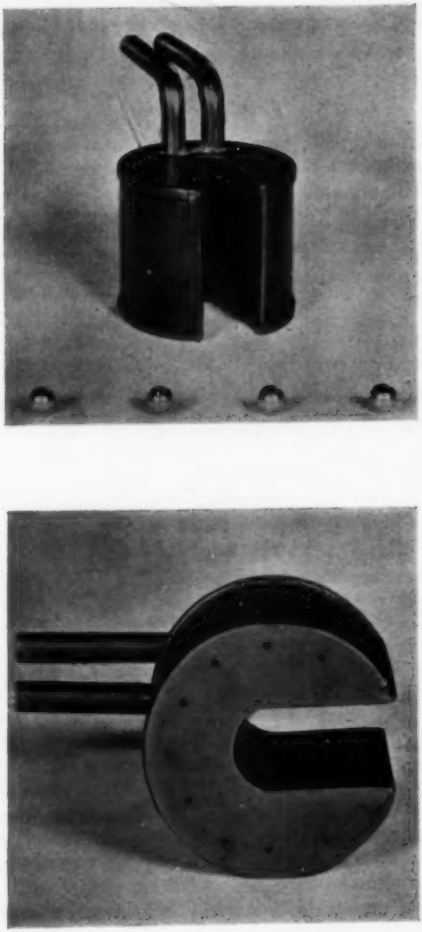

FIG. 14.

LIQUID AIR DISTRIBUTOR.

refrigerant. Nine No. 60 drill holes equally spaced were drilled in the bottom of the evaporator, but eleven of the same size may be necessary for samples containing very large percentages of methane.

Using this arrangement, in conjunction with the other improvements,

methane is easily refluxed and smooth curves and reproducible results accurate to 0·1 per cent. can be obtained consistently. At the same time, operation is both steadier and easier, although operators using it for the first time after liquid gasoline condenser baths will find that much smaller but more frequent additions of liquid air will be necessary. Plateaus are held much longer and, if sufficient boiling and the correct reflux ratio are maintained, the breaks are almost vertical.

Thermocouples.

Three junction No. 26 gauge copper–copper-constantan enamelled-wire couples, calibrated as described previously, were used in conjunction with Englehard Type P millivoltmeters for practically all the work. A L.

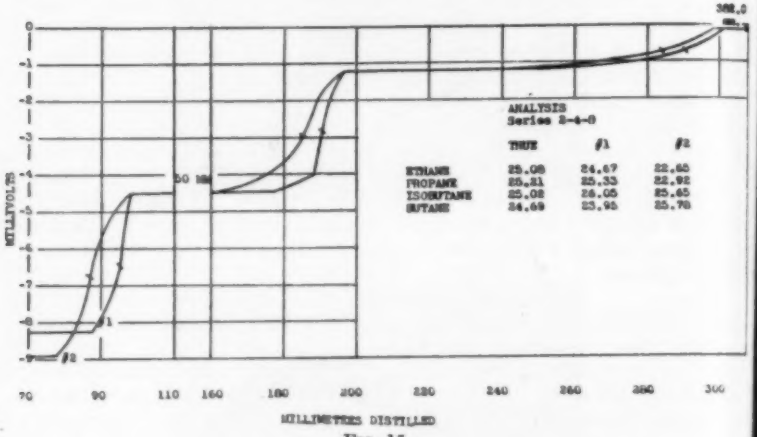

Fig. 15.

Effect of thermocouple position—large tube.

& N. Type K potentiometer gave excellent results when substituted, but added too much complication for the extra accuracy involved. A platinum resistance thermometer was also tried, but was too bulky and required too large a condenser tube.

From the standpoint of accuracy it was found that, so long as the couples were well made, calibrated and treated fairly, they gave results comparable with any other method of measurement, and well within the limits of experimental error without introducing unnecessary complications. Three junctions were preferred to one, on the basis of better accuracy of reading, wider spread of temperatures and the integrating effect of the three junctions.

Far more important than the type of thermocouple is the effect of their position on distillation curves and results.

Fig. 15 shows the effect of two sets of couples spaced 2 inches apart in a condenser tube of large volume. It is immediately apparent that both sets of couples indicated the plateaus at about the correct points, but that the

breaks started first on the lower (No. 2) couples and gave poor curves and results.

The effect of moving the couples in a small tube condenser is shown in Fig. 16. The only difference in the three runs was that the couples were raised 12·5 mm. following each run. It is apparent that only the curves were changed, as all the results were very close to the true percentages of :

Ethane	24·71 per cent.
Propane	25·26 ,, ,,
*Iso*butane	25·32 ,, ,,
Butane	24·71 ,, ,,

Raising the position of the thermocouples cannot be continued beyond a certain point, due to conduction effects from the atmosphere at the upper end of the condenser bath. The best position, using the bead packing as

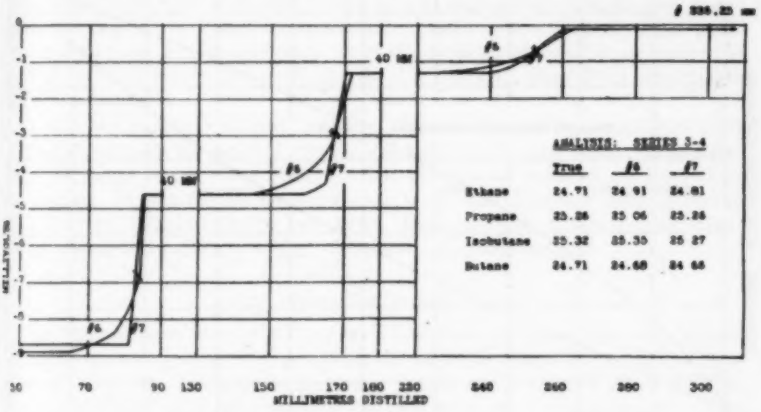

FIG. 16.

EFFECT OF THERMOCOUPLE POSITION—SMALL TUBE.

outlined, is about 7·5 cm. below the rim of the condenser bath, although this may vary 5·0 mm. in either direction, due to individual characteristics of the condensers.

Both soldered and welded junctions were used. The soldered ones were preferred except where extreme care was taken with the welding. In either case the junctions should be as small as possible, and preferably staggered in the space of not over 5·0 mm. in the condenser tube.

MINIMUM SAMPLE VOLUMES.

In spite of a considerable amount of work on minimum sample volumes it is hard to reach any definite conclusions, since the results are erratic and influenced in a large part by the composition of the sample. However, one definite conclusion can be made. It was found that in all cases where the constituent present in least amount was less than approximately 100 ml., poor or inconsistent results were obtained. This was definitely the limiting factor for the heavier ends of distillations to dryness, but not necessarily

the limit for intermediate fractions. That is, if there was considerable material in the kettle at the time a small fraction was being distilled, it would normally be detected and quantitatively separated if the boiling point was not too close to that of another component. However, after the kettle became dry, separation of components of volume less than 100 ml., whether two or more, could not consistently be made within the required accuracy.

Pressure reduction in this case usually produced better separation, primarily by increasing the reflux–vapour ratio, but the amount of fractionation was variable and unpredictable.

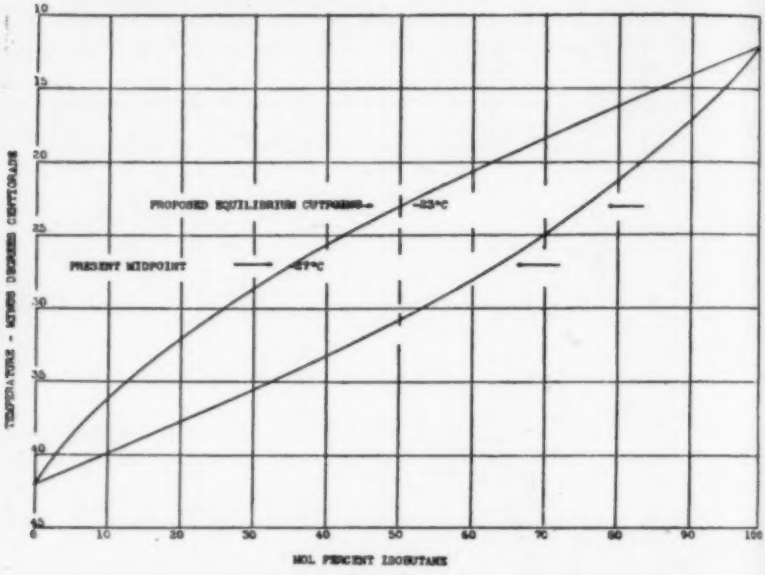

FIG. 17.

PROPANE–*ISO*BUTANE TEMPERATURE—COMPOSITION DIAGRAM.

This means that, if possible, operators should take sufficient gas to ensure at least 100 ml. of each of the final constituents. For an average refinery gas the amount should be about 10 litres; for gases containing higher percentages of heavier constituents a smaller amount can be taken, and for dry natural gases considerably more is necessary.

METHOD OF CALCULATING RESULTS.

At present there are three methods of determining cut-points between the different fractions obtained by fractional distillation.

The most common, known as the mid-point method, takes the cut-point at that temperature which is half-way between the plateaus. Thus, if the one plateau is −88° C. and the other −42° C., the mid-point is −65° C., or half the temperature interval.

The equal area method extends the lines of the plateaus and takes the cut-point where there are equal areas above and below the curves as determined by counting spaces on the cross-section paper. This method was first proposed by Podbielniak, and is standard with the C.N.G.A.

The third method, proposed by Fitch,[4] arbitrarily assigns the cut-point as that temperature at which a 50–50 mol per cent. mixture is in equilibrium in the vapour state. In general, this temperature is several degrees higher than the other cut-point temperatures, as is shown in Fig. 17 for propane–*iso*butane.

It is obvious that in the case of sharp, almost vertical, breaks any of the methods will give good results; but in the case of long slurred breaks there will be a considerable difference, depending on the method used. Inasmuch as it is the temperature of the condensing vapours that is being measured by the thermocouples, it seems more logical that the temperature at which a 50–50 vapour mixture is in equilibrium should be nearer the true cut-point than either the mid-temperature point or the point of equal areas under the curve. Of the latter two methods, neither has any theoretical significance in the separation.

From the results obtained over the whole of the work it was found that equal areas gave the poorest results and took the longest time. In practically all cases it gave low results when the breaks were at all slurred or irregular. Better results were obtained with the mid-point method and in the shortest time, while the best were obtained by equilibrium cut-points which took only slightly longer than the mid-point method.

Deviations from Gas Laws.

Deviations from the perfect gas laws introduce a measurable error unless corrections are applied or provision made for their elimination. It has been found[9] that at atmospheric pressure, beginning with propane, a Boyle's Law deviation of approximately 1·0 per cent. was encountered. This deviation increased rapidly for successively heavier hydrocarbons amounting to approximately 5·0 per cent. for *iso*pentane.

This error can be virtually eliminated from consideration by filling the receivers to only 400 mm. absolute for propane, 300 mm. for the butanes and 100 or less mm. for the pentanes. This does not completely eliminate the error, but does practically equalize it, so that all fractions are in error by the same amount, and hence does not affect the final accuracy.

This error was not encountered in this work, since all pressure measurements were made under similar and reduced pressure conditions.

Comparison of Columns.

After only a comparatively short trial, the glass spiral column under test was discarded, since the results obtained were entirely out of line. The reasons for this failure were threefold. It had too large a volume in the bulbed condenser section, which led to long slurred breaks; the rectifying section of 1·0 metre of 5·0-mm. tubing was entirely too short, and the reflux was difficult to control, since it could not be seen against the clear glass of the spiral. Inasmuch as the only advantage of this type is economy of head-room, it was discarded without further work.

The old " Regular " type one-piece Podbielniak columns were also discarded, primarily because they are no longer manufactured except by special order. Using the new heavy-type packing and a bead packed condenser, they were made to give extremely precise results, almost equal in accuracy to those obtained with the best column. Their only serious disadvantage is that they are extremely fragile, and minor breaks usually require complete rebuilding or replacement.

The old type " L " one-piece Podbielniak precision column is likewise obsolete, and not as satisfactory as the new " micro " precision type.

This leaves only two types for consideration: the Podbielniak " micro " precision and the modified C.N.G.A. developed in this work. Of the two the C.N.G.A gave by far the better results.

Results of four of the best runs on the same sample using the Podbielniak " micro "-column under optimum conditions are shown in Table III.

TABLE III.

Run No.	True.	1.	2.	3.	4.
Per cent. Ethane .	25·08	24·16	24·41	24·18	24·79
" " Propane .	25·21	25·18	25·39	25·95	25·63
" " *Iso*butane .	25·02	24·94	24·61	24·77	24·08
" " Butane .	24·69	25·72	25·59	25·10	25·50

While the results were good, in no case did they approach the accuracy or reproducibility obtained with the modified C.N.G.A. column. Working under optimum conditions of rates, reflux, etc., four distillations on the same sample with the modified C.N.G.A. column showed a maximum deviation of 0·2 per cent. in the butane fraction in two cases and 0·1 per cent. or less for all the others.

Attempts to complete distillations in 2½ to 4 hours with the micro-column as suggested by the manufacturer gave much poorer results, although fairly sharp breaks were still obtained.

Not only were the results better, but the difference in operation also favoured the modified C.N.G.A. type. It was easy to handle, held the plateaus longer, gave sharp smooth breaks with a minimum of lost time and had no tendency to flood. The micro column, on the contrary, had a large time lag in the condenser, with a consequent tendency toward flooding, and in general presented the same difficulties previously encountered with the precision type. Its only advantage over the older precision types is that it operates on slightly smaller volumes and gives sharper breaks. It requires single-junction thermocouples and a special millivoltmeter to obtain the necessary spread for temperature measurements.

Taking into account all the results over the five-year period, considering all the types and modifications of columns tested, their ease or difficulty of operation, and balancing these against their absolute accuracy and reproducibility, it is felt that the best results can be obtained by using a C.N.G.A. type column and accessories as modified and discussed in the foregoing report. Complete details of procedure and specifications for the standardized apparatus will be presented in a subsequent paper.

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COMPOSITION AND CONDUCTIVITY OF OILS AND WAXES.*

By Andrew Gemant.†

Synopsis.

The conductivity–temperature curve of oils and waxes in the melting region allows certain conclusions to be reached as to their composition. For this purpose, a theory is put forward that such systems consist of two phases: a crystalline and a glassy or amorphous one, both having their characteristic conductivities and determining the total conductivity by their volume-ratio. This assumption accounts for the characteristic shape of the curve possessing a pronounced maximum. At the same time the distribution curve of the individual components among the different melting points in the mixture can be deduced. The rigorous construction of the chemical composition would require the knowledge of other physico-chemical data, especially of the equation for the depression of freezing point for concentrated solutions, in absence of which only an approximate computation is possible. In addition, the theory explains the observed dielectric absorption of oils in the transition region.

The theory is developed quantitatively, and three examples of numerical calculation on experimental data are given. These data refer to a lubricating oil, a cable oil and paraffin wax.

(*a*) Statement of the Problem.

It is a well-known fact that changes in the structure of dielectrics at certain temperatures affect, among other characteristics, the conductivity–temperature curves. These curves usually have fairly regular slopes, but at the temperatures mentioned above more or less pronounced discontinuities occur. To be precise, the logarithm of the conductivity is normally a linear function of the reciprocal of the absolute temperature, but the gradient of this straight line suddenly changes at such points.

This effect has been observed in a large number of cases where structural changes are known to occur, so that it is now possible to postulate an alteration in structure from the appearance of discontinuities in the conductivity–temperature curve where no other evidence of such changes is available. Thus from a close study of conductivity it is possible to determine structural changes in dielectrics to some extent.

The purpose of the present paper is to proceed another step. Sometimes the change in slope is not sharp, but varies continuously over an extended region. Generally speaking, we may then deduce not only that a change in structure occurs, but also how it occurs. Such a study is made for oils and waxes.

Three years ago the author showed [1] that the conductivity of oils at low temperatures exhibits a characteristic variation. With decreasing

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† Engineering Laboratory, Oxford University.

temperature it reached a minimum, rose again, and after passing through a maximum decreased continuously. For heavy oils these variations occurred between — 10° and — 50° C., in which region solidification is supposed to set in. Recently W. Jackson [2] observed the same phenomenon with paraffin wax in the region between 0° and 40° C.—that is, in the region where it becomes crystalline. In all these cases we have, therefore, a change in structure and, connected with it, not a sharp, but a very elaborately curved discontinuity in the conductivity curve.

We may conclude from this continuous change that the material does not melt at a particular temperature, but over a certain temperature range. This is quite natural, as we have to deal with a mixture of several constituents. Melting does not occur therefore suddenly, but gradually. We shall show that under certain assumptions it is possible to calculate the melting curve of the material from the conductivity curve. By melting curve is to be understood the curve giving the relative percentage of actually melting components as a function of the temperature. It can easily be seen that if sufficient physico-chemical data concerning the chemical components were available, the actual chemical composition itself could be calculated from the melting curve. As this information is generally lacking, however, we shall have to content ourselves with less exact conclusions concerning the chemical composition.

In spite of this limitation, this will be a fair illustration of the above statement concerning the usefulness of conductivity curves in regard to the structure of the material.

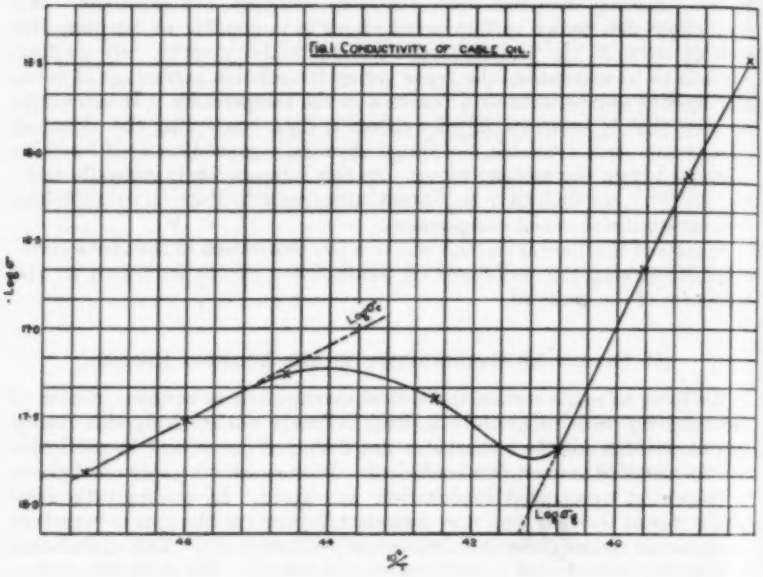
(*b*) Theory of Conductivity in the Melting Region.

We have to make certain theoretical assumptions as to the variation of conductivity with progressive melting. Purely qualitatively this theory has to account for the remarkable flat S-shaped curve, and in particular for the negative temperature coefficient. In the author's paper cited above a somewhat specialized explanation was given. In cooling, the solid phase forms bridges and the adsorbed layers on the phase-boundary increase the conductivity in a certain temperature range. This explanation is possibly correct, but is perhaps too specialized. We shall give here a more general theory, which covers as well the former one.

We give as an example a curve relating to a cable oil of viscosity 100 poise at 35° C. On Fig. 1 the logarithm of conductivity is given as a function of the reciprocal of the absolute temperature. We now assume that the S-shaped part is the melting region; that above, say, — 28° the whole oil is liquid, while below — 46° the whole is solid. However, the oil when below 0° C. is so viscous that it is better to speak of a glassy, or amorphous state, in contradistinction to which the solid may be called the crystalline state. We suppose, then, that in the "melting" region between — 28° and — 46° C. occurs the transition from the amorphous to the crystalline state. If we draw the tangents at both points (dotted lines), we have a good approximation to the behaviour of both the amorphous and crystalline phase just on the limits of the transition region.

It follows from this that our starting point—namely, a continuous transition of a glassy into a crystalline phase—is justified.

Our main hypothesis can now be formulated thus. The conductivity in the melting region is that of a two-phase system, where the respective single conductivities are given by the two tangents at the ends of the said region. This is a formally simple assumption which cannot be exactly true, but it may be used as a guiding hypothesis. We notice at once the rather striking conclusion reached from this assumption, that the extrapolated single conductivity of the solid phase (Fig. 1) is higher than that of the amorphous phase. Usually the contrary is the case; crystals at the melting point have a much lower conductivity than the corresponding liquid. But the molten phase is normally rather fluid, whereas our liquid



phase is, as already mentioned, a glassy one. It is not at all impossible for a crystal phase to have a higher conductivity than its corresponding glassy phase.

Concerning the mechanism of this difference, there are several possibilities. Whether the explanations based on the ideal lattice structure, as, for instance, the place-change theory of V. Hevesy,[5] can account for this is not so sure, at any rate it explains the similar phenomenon with silver iodide. More promising, perhaps, is the real-structure theory of Smekal,[6] which considers the internal voids existing in every real crystal—so-called loose spots—in which loose ions exist having a higher mobility than the lattice ions. The author's former explanation based on the adsorbed ions at the phase boundary is also covered by this general assumption. We shall simply consider the crystalline phase as a whole as having a better conductivity than the glassy phase; whether this is due to the lattice

structure, to internal loose spots, or only adsorbed ions, is a secondary question. Important only is the fact that the assumption follows from the general behaviour of the experimental curves as shown in Fig. 1; the extrapolated conductivity of the glassy phase is in the transition region always below that of the crystalline phase. It explains, without any constraint, the curious intervening maximum, as will be shown later.

A different explanation is suggested by F. C. Frank, who considers only the glassy phase. During the process of melting the viscosity of the liquid phase would experience a certain increase, owing to the fact that more and more of the higher-melting components go into solution. We could roughly imitate this fact by considering the viscosity of a paraffin–benzene mixture during the melting of paraffin. As a result of this, the decrease of conductivity during the melting period is understandable.

This explanation is rather attractive, and on its basis the construction of the melting-curve could as well be effected as on the basis on the theory outlined above. As there is no strict point of evidence for either of them we shall work out the following on the basis of the two-phase theory, since the mathematical treatment proves extremely simple. Moreover, it evidently allows certain conclusions on dielectric absorption in the transition region to be drawn.

(*c*) Calculation of the Melting Curve.

(i) *Two-Phase Theory.*—We define the melting state in the transition region by a quantity n, which denotes the ratio of the volume of crystalline

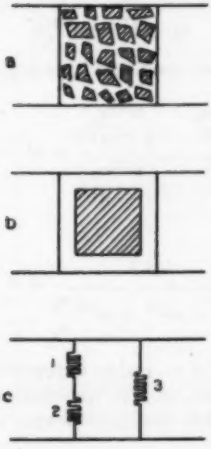


Fig. 2. Model of oil in melting range.

phase to the total volume. If we know n as a function of temperature, we have at the same time the melting function, the former being (as we will show below) the integral of the latter. What is given by experiment is

the conductivity σ as a function of temperature. The only thing to do is to establish a relation between σ and n, and the problem is solved.

In order to find the relation of σ to n, let us consider a unit element of volume of the dielectric located between two parallel condenser plates (Fig. 2 (*a*)). We suppose the crystallites, schematically shown in the figure, to be interspersed in the amorphous phase. For the computation of the electrical resistance we simplify the case by packing all the crystals together in a cube and identifying the real structure with the simpler one shown in Fig. 2 (*b*). We notice that the identity is only an approximation, as the real field distribution must be different in the two cases.

The arrangement Fig. 2 (*b*) is now equivalent electrically to the circuit shown on Fig. 2 (*c*), consisting of two resistances, 1 and 2, in series; and one, 3, parallel. According to definition the volume of the inner cube on Fig. 2 (*b*) is n, each of its surfaces being $n^{2/3}$ and the side-length $u^{1/3}$. The conductivity of the resistance 1 is therefore

$$\sigma_1 = \frac{n^{2/3}\sigma_c}{n^{1/3}}$$

if σ_c denotes the specific conductivity of the crystalline phase. Similarly, for the resistance 2

$$\sigma_2 = \frac{n^{2/3}\sigma_g}{1 - n^{1/3}}$$

if σ_g denotes the specific conductivity of the glassy or amorphous phase. For resistance 3 we have

$$\sigma_3 = (1 - n^{2/3})\sigma_g$$

In consequence, the resultant conductivity σ is given by

$$\sigma = \frac{\dfrac{n^{2/3}\sigma_c}{n^{1/3}} \cdot \dfrac{n^{2/3}\sigma_g}{1 - n^{1/3}}}{\dfrac{n^{2/3}\sigma_c}{n^{1/3}} + \dfrac{n^{2/3}\sigma_g}{1 - n^{1/3}}} + (1 - n^{2/3})\sigma_g$$

or, in re-arranged form

$$\sigma = \left(\frac{n^{2/3}}{(1 - n^{1/3} + n^{1/3}\dfrac{\sigma_g}{\sigma_c}} + 1 - n^{2/3} \right) \sigma_g \quad . \quad . \quad . \quad (1)$$

It can be seen that for $n = 1$ this expression becomes σ_c, whereas for $n = 0$ it becomes σ_g. Now, in the denominator of this expression the last term $n^{1/3}\,\sigma_g/\sigma_c$ is normally negligible owing to the fact that

$$\sigma_g \ll \sigma_c$$

It is easy to show when this approximation is no more justified. This will be the case when

$$n^{1/3}\frac{\sigma_g}{\sigma_c} \approx 1 - n^{1/3}$$

that is, for values of n very near unity. Writing

$$a = 1 - n,$$

we have

$$\frac{\sigma_g}{\sigma_c} \approx \frac{1 - (1-a)^{1/3}}{(1-a)^{1/3}}$$

If $a \ll 1$, this becomes

$$\frac{\sigma_g}{\sigma_c} \approx \frac{a}{3}$$

or

$$\frac{\sigma_g}{\sigma_c} \approx \frac{1-n}{3}$$

As σ_g/σ_c is generally not greater than 10^{-3}, the simplified equation will hold for

$$n < 0{\cdot}99,$$

that is, practically in the whole transition range.

With this small restriction, formula (1) may be written

$$\sigma = f\sigma_g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where f denotes the function

$$f = \frac{n^{2/3}}{1 - n^{1/3}} + 1 - n^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Fig. 3 gives $\log f$ as a function of n. Equation (2) is the relation we sought.

Equations (2) and (3) show that with decreasing temperature the con-

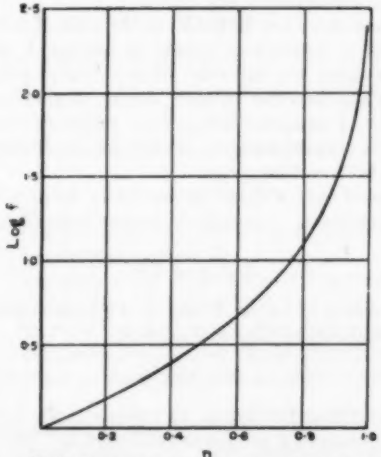


FIG. 3. VARIATION OF f WITH CRYSTAL VOLUME.

ductivity decreases so long as n is zero and $f = 1$. From the start of devitrification n increases, as well as f, and the resulting conductivity σ

must rise. From the point $n = 1$ onwards, σ becomes σ_e and accordingly decreases again.

In order to deduce the melting curve $n(t)$, the function $\sigma_g(t)$ has to be known. For a given experimental curve, the slope of the logarithmically plotted curve above the melting range gives the function $\sigma_g(t)$.

The slope below the melting range, on the other hand, gives $\sigma_e(t)$, the knowledge of which, however, is not necessary in this connection. It will prove important for the calculation of the absorption.

The experimental data $\sigma(t)$ in the melting range allow at once evaluation of the $n(t)$ curve.

In addition, it should be mentioned that the calculation may be refined if required. In particular, the calculation of σ from n is capable of improvement. As the real shape of the crystallites is unknown, it is not possible to compute the real field distribution. The crystals have been considered here as little prisms interspersed in the glassy medium and as being equivalent with one large cube of the same volume. It is just as well to consider them as small spheres. The computation in this case can be based on the corresponding work of Maxwell.[7] Investigating this case, he found for $n \ll 1$ in our notation

$$\sigma = \frac{2\sigma_e + \sigma_g + n(\sigma_e - \sigma_g)}{2\sigma_e + \sigma_g - 2n(\sigma_e - \sigma_g)}\sigma_g$$

which may be used instead of equation (1). As n becomes larger, this equation has to be replaced by a more general one.

(ii) *Bridge Theory.*—Before proceeding with numerical calculations on this basis, we intend to show the analogous theory based on the more special assumption already alluded to—namely, that it is the interfacial conductivity which accounts for the effect.

Let us assume that there are $3k$ nuclei in the unit of volume, each leading to the formation of a crystalline thread or bridge, k, in each dimension (considering the bridges, for the sake of simplicity, perpendicular to the main surfaces). They become thicker during crystallisation, until they fill the whole space; k separate bridges are therefore connecting the electrodes and adding a certain amount of surface conductivity, owing to adsorbed ions, to the bulk conductivity.

The cross-section of one of these bridges may be denoted by q, which is a function of temperature; q increases during crystallization from zero to $1/k$,

$$0 < q < 1/k.$$

The conducting surface of each thread is $4\sqrt{q}$ (assuming a square cross-section), and the total conducting surface S is

$$S = 4k\sqrt{q}.$$

It is possible, on the other hand, to calculate the total volume of the crystals n. The volume of k prisms is evidently kq; the additional volume of the prisms in the two perpendicular dimensions will be less, as they intersect with the first set of bridges. There are $\sqrt{k}$ bridges of the first set, intersecting with each prism of the two other sets. The ratio of volume taken by these $\sqrt{k}$ bridges to the total volume of one is $\sqrt{kq}:1$. The

additional volume of each set is therefore $kq(1 - \sqrt{kq})$, and the total volume n is given by

$$n = kq + 2kq(1 - \sqrt{kq}) = kq(3 - 2\sqrt{kq}).$$

This is zero for $q = 0$, and becomes unity for the limiting case $q = 1/k$, as it ought to be. Eliminating q, we get

$$n = \frac{S^2}{16k}\left(3 - \frac{S}{2\sqrt{k}}\right)$$

or, introducing the new variable

$$x = \frac{S}{4\sqrt{k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$n = x^2(3 - 2x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now the total conductivity σ is given by the bulk conductivity σ_0, and the surface conductivity $S\sigma_s$, if σ_s denotes the specific surface conductivity

$$\sigma = \sigma_0 + S\sigma_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Equations (4), (5) and (6) give the relation between n and σ; (6) shows again clearly the peculiar shape of the curve.

From (6) we have

$$S = \frac{\sigma - \sigma_0}{\sigma_s}$$

and as we need x for evaluating n, we write

$$x = \frac{\sigma - \sigma_0}{4\sqrt{k}\sigma_s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Now the slope of the curve above the melting region ($S = 0$) gives immediately

$$\sigma = \sigma_0$$

hence $\sigma_0\,(t)$. The curve below the melting range ($S = 4\sqrt{k}$) gives

$$\sigma = \sigma_0 + 4\sqrt{k}\sigma_s$$

hence $\sqrt{k}\sigma_s\,(t)$; x is therefore known (from 4a) as a function of the temperature, and $n\,(t)$ can be computed from (5).

(iii) *Numerical Computation on Experimental Curves.*—The first of the outlined theories, based on the two-phase system, should be used for numerical evaluations. As may be seen from the foregoing deductions, the knowledge of the slope above the melting range, corresponding to the liquid phase, is very important. However, this slope must be drawn somewhat arbitrarily.

The following suggestion might be useful. Measurement on oils at low temperatures are better carried out with increasing temperature (as was found in the author's investigation), since the points are more likely to represent stable states, than with decreasing temperature. In this latter case the liquid shows a tendency to super-cooling; but in spite of this,

it is better to take both curves. The curve with increasing temperature may serve to give corresponding values of σ and t, whereas the other curve supplies the function $\sigma_g(t)$ with a higher degree of certainty.

1. *Cable Oil.*—The following is the calculation concerning the curve on Fig. 1 already mentioned. Here the variation on both sides of the melting

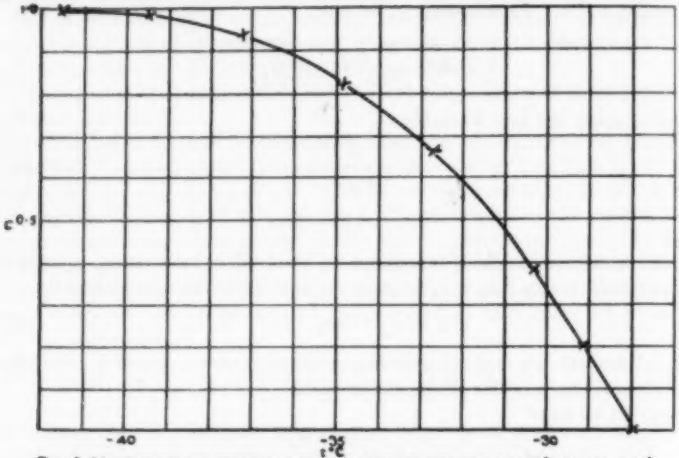


FIG. 4. VARIATION OF CRYSTAL VOLUME WITH TEMPERATURE (CABLE OIL).

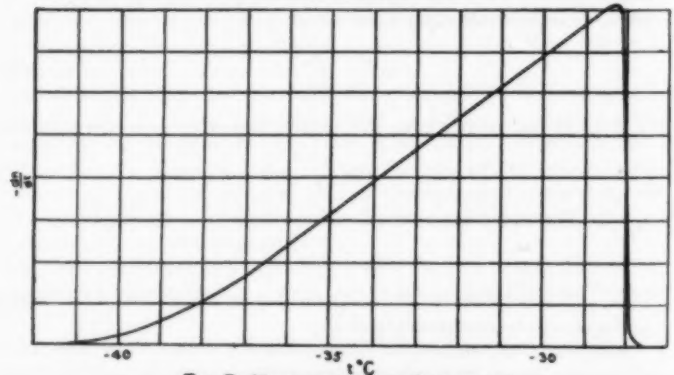


FIG. 5. MELTING CURVE (CABLE OIL).

region is quite linear, so there is little doubt as to the numerical value of the slope. For the glassy phase the following equation holds

$$\log \sigma_g = 16{\cdot}55 - 0{\cdot}89\,\frac{10^4}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where T is the temperature in Kelvin degrees. The corresponding equation for the crystalline phase is

$$\log \sigma_c = -\,7{\cdot}69 - 0{\cdot}21\,\frac{10^4}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

The calculation itself is given in Table I. The first column contains the reciprocal of the absolute temperature, the second t, the corresponding temperature in ° C. The third column is the value for $\log \sigma$ as read directly from Fig. 1. The fourth column is $\log f$, as calculated from (2), the corresponding values for σ_2 being given by (7), which is considered true in its extrapolated region. The fifth column gives n as read from Fig. 3; n as a function of t is shown on Fig. 4.

TABLE I.

Calculation of Melting Curve for a Cable Oil (Fig. 1).

$10^4/T$.	t° C.	$\log \sigma$.	$\log f$.	n.
43·6	−43·6	−17·21	3·0	~1·0
43·2	−41·5	−17·25	2·64	0·995
42·8	−39·4	−17·32	2·22	0·985
42·4	−37·2	−17·43	1·76	0·94
42·0	−34·9	−17·57	1·26	0·81
41·6	−32·6	−17·69	0·78	0·66
41·2	−30·3	−17·75	0·37	0·38
41·0	−29·1	−17·75	0·19	0·20
40·9	−28·5	−17·73	0·12	0·14
40·8	−27·9	−17·69	0·0	0·0

As the value of n gives the amount of crystalline phase at the temperature t, the value $-dn/dt$ gives the amount crystallizing in the interval between t and $t + dt$. The differential coefficient of Fig. 4 is therefore the

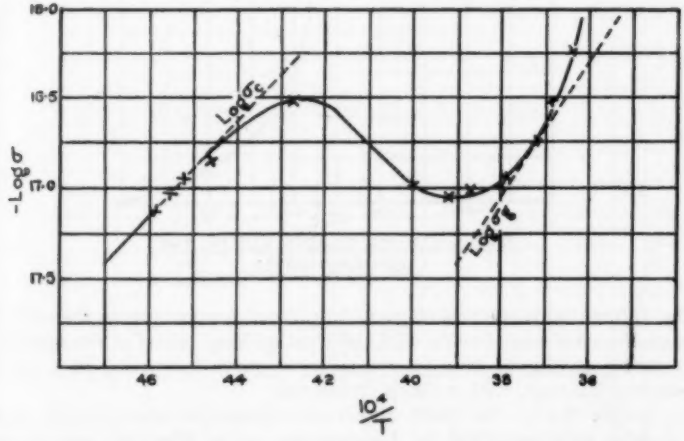


FIG. 6. CONDUCTIVITY CURVE FOR LUBRICATING OIL.

melting curve sought. It is shown on Fig. 5. Crystallization starts rather sharply at − 28° and continues at a linearly decreasing rate until − 42° C.

2. *Lubricating Oil.*—We proceed now to deduce the melting curve corresponding to the experimental conductivity curve of Fig. 6. It corre-

sponds to a heavy oil, having a viscosity of 140 poise at 20° C. The fixing of the slope at the upper limit of the melting region was here rather arbitrary. The result is probably not too greatly affected by the choice of this limit.

From the equations for the dotted lines we find for the conductivity of the crystalline phase

$$\log \sigma_c = -4{\cdot}7 - 0{\cdot}27\,\frac{10^4}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and for the glassy phase

$$\log \sigma_g = -3{\cdot}3 - 0{\cdot}36\,\frac{10^4}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

The result, namely, n as a function of the temperature in ° C., is plotted on Fig. 7. We see that it is a fairly symmetrical curve.

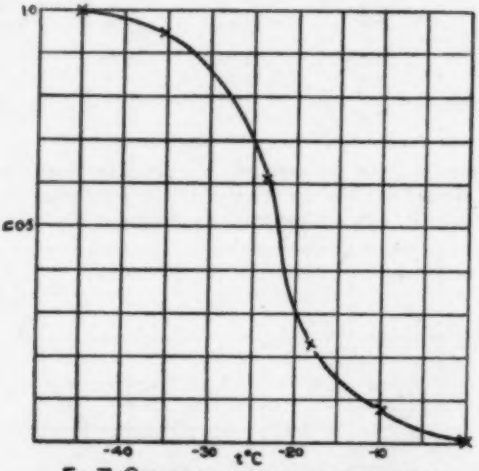


FIG. 7. CRYSTAL VOLUME CURVE FOR LUBRICATING OIL.

The differential coefficient of curve Fig. 7 is the curve giving the relative concentrations of components with different melting points in the mixture. It is shown on Fig. 8, being a symmetrical curve increasing in a nearly exponential manner, with a sharp maximum.

3. *Paraffin Wax.*—The third numerical calculation refers to the curve for paraffin wax published by Jackson (*loc. cit.*). The data are plotted logarithmically on Fig. 9. It has the great advantage of having been taken in both directions, curve *a* referring to increasing temperatures, curve *b* to decreasing temperatures. The main deviation between both is located on the left part of the curves, the down curve exhibiting the lower figures. This fact is in agreement with the theory. It is certain that the system in curve *b* contains a considerable amount of supercooled glassy phase,

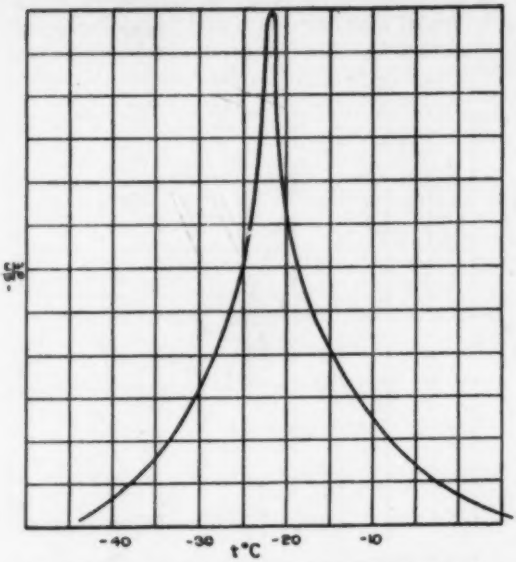
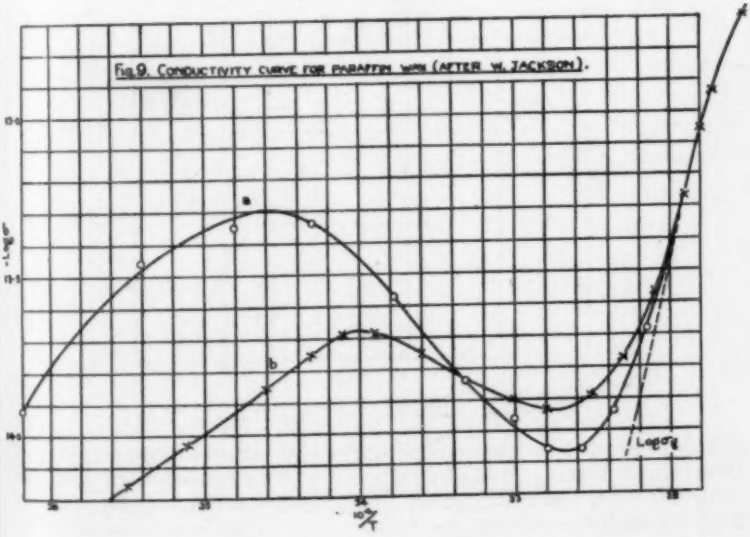


FIG. 8. MELTING CURVE FOR LUBRICATING OIL.



thus decreasing the resulting conductivity. On the other hand, the slope for σ_g (t) can be traced with more certainty. Both curves coincide in this region. The tangent at the inflection point is probably the best adapted for σ_g (t). A smaller value for the slope, corresponding to lower temperatures, is

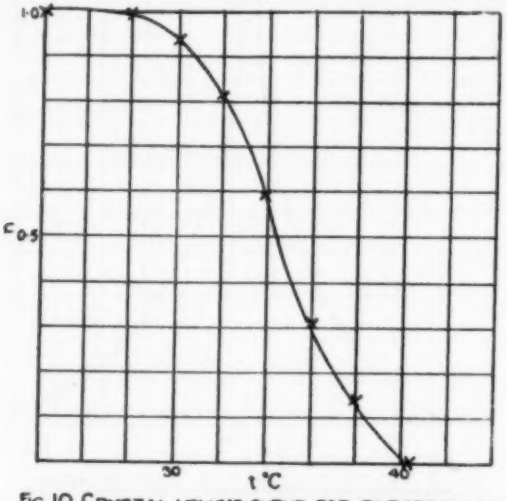


FIG. 10. CRYSTAL VOLUME CURVE FOR PARAFFIN WAX

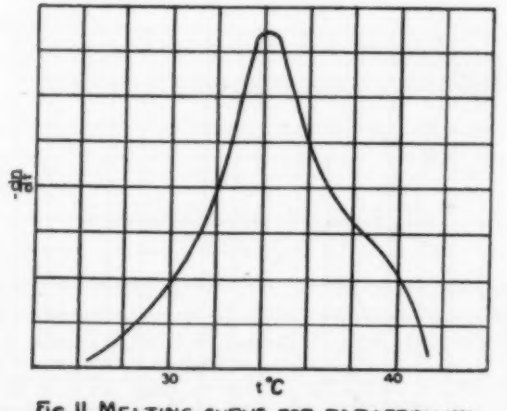


FIG. 11. MELTING CURVE FOR PARAFFIN WAX

certainly incorrect, as here the departure of both curves indicates that crystallization has begun. A smaller value for the slope corresponding to higher temperatures is improbable, as it would mean a relative decrease of the resulting conductivity compared with σ_g, which is not accounted for by the theory.

For σ_g, therefore, the following function has been chosen

$$\log \sigma_g = 56{\cdot}3 - 2{\cdot}18 \frac{10^4}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The n (t) curve is given on Fig. 10 and the melting curve on Fig. 11. It does not start so sharply as the curve Fig. 8, and is not so symmetrical as Fig. 5.

(*d*) Conclusions Regarding Composition.

The conclusions as to chemical composition which can be reached from the melting curve must next be considered. Were the mixture under consideration composed of several components differing widely in chemical composition, the answer would be rather difficult. The constituents of an oil, however, are all similar in structure, being usually neighbouring members of a homologous series. This circumstance simplifies somewhat the case, but even so the conclusions reached are not rigorous, only informative, but capable of gradual improvement.

The crucial question is whether the melting points indicated on the curves can be identified with the melting points of pure individuals of the homologous series to which the oil belongs. In this case the evaluation of the composition would be very easy. We shall show, however, that this is justified only as a first approximation.

(i) *Thermodynamical Considerations.*—We have to deal with a mixture of several hydrocarbons, and it can be proved for such mixtures thermodynamically that the melting points of the components suffer a mutual reduction. The temperatures indicated on the curves will be lower than the freezing points of the respective pure components.

Denoting the gas content by R, the melting point of the solvent by T_0, the percentage of the solute by m, the molar heat of fusion of the solvent by h_m and the molecular weight of the solvent by M, we have :

$$t = \frac{RT_0^2}{100\, h_m} \frac{m}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This equation of van 't Hoff permits the calculation of the order of depression of the freezing point. h_m is about 50 cal. (for instance, 44 cal. for palmitic acid; 51 cal. for stearine), M is, on the average, say 200. This means that the depression for a 10 per cent. solution is about 2° C. Owing to the high molecular weight of the higher hydrocarbons, the depression is rather limited.

In such mixtures one after the other will crystallize with decreasing temperature, commencing with the component with the highest freezing point. This does not occur sharply, however, but gradually, yielding melting curves such as have been found in the foregoing section.

In a case of only two components, the higher melting one should be called the solvent, the other the solute. The solvent starts to crystallize, increasing the concentration of the solution and further depressing the freezing point. If the solution is not too concentrated, and equation (10) holds, we have for the temperature at which crystallization commences

$$T_0 - \frac{RT_0^2}{100\, h_m M} m_0$$

if m is the initial percentage of the solute. Each new concentration is connected with a lower freezing point. Thus, if 100 n percentage solvent has frozen out, the new concentration is

$$m_0 \frac{1}{1-n}$$

and the temperature, belonging to this equilibrium

$$T = T_0 - \frac{RT_0^2}{100\, h_m\, M}\, m_0 \frac{1}{1-n} \quad . \quad . \quad . \quad . \quad (11)$$

This equation would describe in this case the right-hand portion of the $n(t)$ curve. That is, however, only an ideal case. The real one differs from it in that the solution contains more than two components, crystallizing together as solid solutions, and that their concentration is much higher than the allowable limit for equations valid for dilute solutions. It seems that a special investigation on hydrocarbons is required in order to determine the general equation, replacing (10), which should be valid for any concentration.

The knowledge of the general equation will make it possible to reconstruct the composition curve more exactly.

Evidently each component can be considered as solvent. For each an equation similar to (11) will hold. Suppose there are q components, each having its initial concentration m, its freezing point T_0, and its crystal fraction n_m. Each—let us call it the ith component—will have to fulfil an equation of the form

$$T = T_0\, i - \frac{RT_0^2}{h_m\, M}\, \phi \left\{ \frac{\sum^{q(i)} m(1-n_m)}{\sum^{q} m(1-n_m)} \right\} \quad . \quad . \quad . \quad (12)$$

here the bars stand for average values, ϕ is the general function just mentioned, the summation $q(i)$ has to be extended over all the components except the ith, the summation q over all of them, the bracket being therefore the concentration of all other components in the ith.

These are q equations, with q unknowns n_m, and as

$$n = \frac{\sum^{q} m n_m}{100}$$

the curve n (t) can be constructed. Beginning with the approximate solution it is only necessary to improve the values of m, corresponding to the different T_0 until the solution of the q equations fits perfectly the observed curve. As its construction is in steps, beginning from the right-hand end with only one equation, always adding one more as the different T_0 are passed, the evaluation of the total system of the q values of m is not so difficult as might appear at first sight.

(ii) *Approximate Method.*—The general equation not being available, an approximate method is proposed. First the homologous series in question must be known. Consider, for instance, the well-known paraffin series. A knowledge of the melting points of the pure members in that series is next required.[8]

The curve relating the melting points with the number of carbon atoms is here, as in many other cases, a zig-zag line, a given smooth curve being valid for both the even and odd numbers of carbon atoms.

An allowance has to be made for the shift of the whole range, for the reason mentioned above. The corresponding curve of melting points of the pure components will be shifted towards the right at the upper limit of the curve. The lower limit has not to be shifted, as in that range all other components are already frozen out, so that the material can be considered as a pure one. The order of shifting of the upper limit will be, as has been shown above, a few degrees, say, 10° C.

Having thus fixed the members of the series, ranged along the abscissa according to their melting points, the area described by the melting curve above the different portions of the abscissa will give a measure for the relative concentrations of the components. The result of this estimate for the cable oil and paraffin wax is given in Table II.

TABLE II.

Approximate Composition Data.

Chemical Compound.	Cable Oil, %.	Paraffin Wax, %.
$C_{10}H_{22}$	35	
$C_{11}H_{24}$	65	
$C_{12}H_{26}$		15
$C_{20}H_{24}$		35
$C_{21}H_{44}$		35
$C_{22}H_{46}$		15

The figures represent the percentage of the corresponding components in the mixture. The Texas oil has been left out from this computation, as it consists mainly of cyclic hydrocarbons. But an extension of the calculation to any known series—that is, to any kind of oils—offers no special difficulties.

(*e*) DIELECTRIC ABSORPTION IN THE TRANSITION REGION.

As mentioned above, the two-phase theory immediately leads us to the mechanism of absorption in the melting region. In his paper cited above, the author observed very large anomalous charging currents, so that reliable measurements of conductivity were possible only after the D.C. potential had been applied for more than a quarter of an hour.

W. Jackson has measured absorption currents in paraffin wax (*loc. cit.*) and found a pronounced maximum near the transition region. P. P. Kobeko and co-workers [10] find in their recent investigations a direct correlation between certain absorption maxima and softening region.

In the expression for the absorption current density i_a for the unity of of field,

$$i_a = i_0 e^{-t/\tau}$$

i_0 is the absorption constant, and τ the time constant.

The absorption constant is given by

$$i_0 = n^{2/3}\left[(1-n^{1/3})\sigma_g + n^{1/3}\sigma_c - \frac{1}{\frac{1-n^{1/3}}{\sigma_g} + \frac{n^{1/3}}{\sigma_c}}\right] \quad . \quad (13)$$

and the time constant by

$$\tau = \frac{\epsilon}{4\pi}\frac{1}{n^{1/3}\sigma_g + (1-n^{1/3})\sigma_c} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

(where ϵ = dielectric constant)

TABLE III.

Dielectric Absorption Data for Lubricating Oil.

Temperature in ° C.	a_0 in mho/cm.		τ in seconds.		i_a in amperes for $t = 10^3$ sec.	
−50	0		—		0	
−35	0·76	10^{-16}	83	10^3	0·75	10^{-16}
−23	1·8	10^{-16}	3·4	10^3	1·3	10^{-16}
−18	1·4	10^{-16}	0·67	10^3	0·32	10^{-16}
−10	0·9	10^{-16}	0·22	10^3	0·011	10^{-16}
− 3	0		—		0	

With increasing temperature, the time constant decreases continuously, the current for a given time going through a maximum. The order of the time constant (10^3 seconds) agrees well with the observation of the author; their numerical value is perhaps higher than those observed.

A direct comparison with the experimental values is difficult, inasmuch as other mechanisms may overlap the one in question, especially on the crystalline side of the range.

The author wishes to acknowledge his best thanks to the E.R.A. for its aid in enabling him to carry out this work, to Professor R. V. Southwell and Mr. E. B. Moullin of the Engineering Department for their kind hospitality, and to his colleague W. Jackson for his stimulating discussion of the topic.

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TRENDS IN THE MANUFACTURE AND USE OF LUBRICATING OILS.*

By Oswald Bell, B.Sc.

Until the latter half of last century, lubrication was carried out entirely with animal or vegetable oils, but with the modern industrial tendencies for high-speed machinery operating continuously for lengthy periods the requirements are for lubricants of lower cost and greater stability.

The deciding influence which the internal-combustion engine has exercised on lubricating oil manufacture is attributed to three factors :—

1. The very varied duties in the engine which have to be performed by the one oil.
2. The increasing consumption of lubricants by the internal-combustion engine; amounting to over 50 per cent. of the total lubricant production in the U.S.A.
3. The critical attitude of the average automobile owner, who is liable to attribute any failure of the machine to faulty lubrication.

A comparison of the general characteristics of paraffin-base and naphthenic-base oils indicates the general trend of lubricating oil manufacture. Apart from general tests such as Carbon Residue, Flash Point, etc., the present tendency is to emphasize the importance of viscosity–temperature sensitivity, and the Viscosity Index of Dean and Davis which has been developed for this purpose gives characteristic values for oils from different crudes, *i.e.* Pennsylvanian oils, 100; Mid-Continent oils, 80; Texas, about 10; Coastals, as low as minus 140. Rumanian oils range from about 50 to minus 40 according to origin. It is suggested, however, that naphthenic oils may possess increased "oiliness" to counteract their poor V.I., but improvements in V.I., carbon residue, and oxidation or sludging stability have been responsible for the general adoption of solvent refining processes. On the other hand, there has been no real tendency towards improved oiliness, although R. O. King has shown that certain blends of naphthenic and paraffinic oils have better lubricating value than paraffinic oils alone.

Other tendencies are :—

1. The use of lower viscosity oils.
2. Rationalization of nomenclature by adoption of S.A.E. Standard.
3. The use of dopes for various purposes, such as pour point depressors, anti-oxidants, etc., which, however, are not of outstanding importance.

rom the manufacturing standpoint, the outstanding development has oubtedly been the introduction of solvent processes; although the reasing use of high-vacuum distillation units, such as the Dry Vacuum

*Précis of paper read before the Rumanian Branch of the Institution of Petroleum nologists, November 22nd, 1935.

Process developed for Mid-Continent and Californian oils in which the oils are stabilized with caustic soda and distilled without steam, should be mentioned.

The two aspects of solvent refining are: (*a*) Solvent Extraction; and (*b*) Solvent Dewaxing. The purpose of the first is to segregate the desirable constituents of the base stock, which may be done by a single-solvent, or by a double-solvent process, although the latter is more generally applied to the refining of residuals. In general practice, counter-current methods are employed, and the process is very analogous to distillation in principle.

For the new Solvent Dewaxing processes, the advantages claimed are greater flexibility in cooling rates, and the ability to obtain lower pour points with the same degree of cooling. Typical solvents are: (1) Chlorinated Hydrocarbons, which have an added advantage in non-inflammability, (2) Acetone–Benzole, and (3) Propane.

Regarding the use of solvent processes in Rumania, it is realized that these are chiefly applicable to the manufacture of motor oils, and while more than 50 per cent. of the total lubricants manufactured in the United States are motor oils (the equivalent percentage for English markets is about 20 per cent.) in Rumania only 5–7 per cent. of the oil consumption is for automobiles. Freight charges would hamper production for export, whilst solvent costs and availability would differ considerably from American figures. Moreover, it is doubtful, in view of the high paraffin and low oil contents of Rumanian paraffinous crudes, if reasonable yields could be obtained.

DETERMINATION OF CRITICAL TEMPERATURE AND PRESSURE OF PETROLEUM FRACTIONS BY A FLOW METHOD.*

By Louis C. Roess, E.E., Ph.D.†

Introduction.

Comprehensive critical temperature and pressure data for petroleum fractions are of real value in the estimation of P-V-T relations [11] and in the study of petroleum refining operations where knowledge of phase conditions may be important. The critical volume is not so important, because its value varies over only a small range, and can be estimated from a knowledge of the critical pressure and temperature.

In the past, the critical constants have been determined by means of a static method in which the substance is held at its critical point for an appreciable time. It is this unavoidable feature of the static method which causes its failure when applied to a substance, such as a gas oil, which decomposes at its critical temperature. In general, due to this decomposition or cracking, the observed critical temperature is less than the true value for the original substance, while the observed critical pressure is greater than the true value. Because experimental conditions prevent the measurement of the amount of decomposition, it is not possible to determine just what substance actually is being measured. The application of this method to petroleum fractions is therefore limited to those having critical temperatures below 850° F., when only the critical temperature is measured, and to those having critical temperatures below 700–750° F., when all the critical constants are being measured.

It is clear that a flow method, in which the oil is heated very rapidly to its critical temperature, would eliminate the faults of the static method. To make a flow method successful, two problems had to be solved:

(1) A chamber in which the flowing oil could be observed visually at high temperatures and high pressures had to be developed.

(2) A positive method of identifying the critical point of the flowing oil had to be devised or discovered.

This article describes the solution of these two problems and presents critical data obtained on over one hundred petroleum fractions.

Previous Research—Critical Temperature.

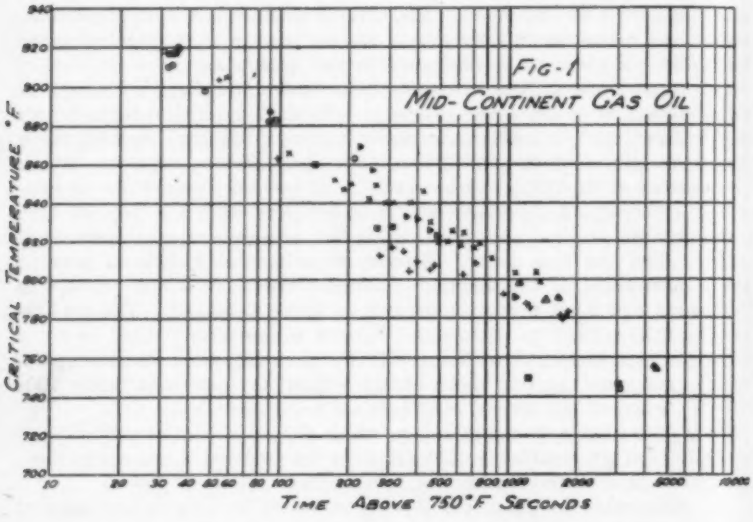
The most important published work on the critical temperature of petroleum fractions is that of Eaton and Porter.[3] Other workers who have published critical temperature data are Zeitfuchs,[1] McKee and Parker,[2] McKee and Szayna,[4] Weir and Eaton,[5] and Bahlke and Kay.[6]

* Paper received August 8th, 1936.

† Beacon Laboratory of The Texas Company.

All these critical temperature data have been obtained by a static method similar to that of Eaton and Porter. In their method a 5–7 mm. pyrex tube about 1 inch long is filled one-third full of oil and then sealed off. A thermocouple is then fastened to the outside of this capsule, and the whole is placed in a suitable furnace, in which it is heated to the critical temperature, the oil being thoroughly stirred by rotating the capsule. The critical temperature is taken as that at which the oil meniscus vanishes somewhere near the middle of the capsule. This last condition is fulfilled by filling the capsule with the proper amount of oil, the result being unaffected by a plus or minus 10 per cent. variation in the cold oil volume.

Using these data and that of others on pure compounds, Eaton and Porter developed a correlation between the critical temperature, the A.S.T.M. 50 per cent. point, and the density. This correlation has been



used extensively by the petroleum industry. The present work shows that it predicts critical temperatures correctly up to about 800° F., above which the predicted critical temperatures are too low, as would be expected from the fact that appreciable cracking, with consequent reduction in the critical temperature, must have occurred during the long contact times (60–120 seconds) at cracking temperatures, which are necessary for measurements by the static method.

In the initial critical temperature investigations carried out in this laboratory a static apparatus similar to that of Eaton and Porter was used. It was found that almost any result could be obtained for the critical temperature of any oil which cracked appreciably at its critical temperature, simply by varying the length of time taken to heat the oil from 750° F. to its critical temperature. If this time was short, the thermocouple heated more rapidly than the oil, giving too high an apparent

critical temperature; while if the time was long the oil cracked, giving too low an apparent critical temperature. These statements may be verified by referring to Fig. 1, which shows the effect of time above 750° F. on the observed critical temperature. The points represented by circles are values obtained with different capsules, while all the other points were obtained by maintaining the oil near its critical temperature and taking readings at intervals. Thus, on Fig. 1 the squares, triangles, crosses, and plus signs represent data obtained in this manner on four different capsules. One reason for the large spread of the data is that no effort was made to keep the temperature from run to run exactly the same between readings, so that the different runs are not strictly comparable on a time basis. The predicted critical temperature for this oil is 900° F. according to the correlation proposed in this article.

The difficulty with the static method just described and exemplified cannot conceivably be overcome by modifications in the apparatus, since even if the thermocouple temperature could be made the same as the oil temperature for rapid heating rates, the rate of temperature rise (the range from 750° to 900° or 1000° F. must be traversed in less than one second) necessary to prevent cracking could not possibly permit an accurate observation or temperature measurement.

Previous Research—Critical Pressure.

Very little data on the critical pressure of petroleum fractions have been published. Bahlke and Kay [6] have measured the critical pressure of a gasoline and a naphtha, employing a static method similar to that used for critical temperature measurements except that the pressure in the capsule is transmitted to a gauge by means of mercury. The maximum temperature at which accurate measurements can be made is even less with the critical pressure determination than with the critical temperature determination because more time is required. It is certain that this method is not accurate above 700–750° F.

Need for New Method.

The almost total absence of critical pressure data, and the lack of critical temperature data in the high temperature region, emphasized the need for a new method of measurement which would eliminate the effect of cracking. This necessity suggested measuring the critical temperature and pressure by a flow method, since previous experience (unpublished) with cracking equipment had shown that it was possible to heat the oil to its critical temperature while flowing, without the occurrence of appreciable cracking. It was clear that the success of such a method depended on the ability to observe some phenomenon which would define the critical point during flow.

The Critical Phenomena.

The static method uses the vanishing of the meniscus between the liquid and vapour phases of the oil as an indicator of the critical point. Obviously, this change cannot be used when the oil is flowing. To determine what

phenomena could be used to identify the critical point during flow, a preliminary experiment, in which flowing pentane was heated under pressure in a long pyrex tube, led to the thought that the critical point could be identified by means of a fine mist which could be made to appear and disappear by varying the pressure up and down through the critical pressure. Later work showed that this phenomenon was not sufficiently definite, particularly for wide-boiling mixtures, and a much more certain indicator was used.

This indicator was a very definite colour change in the flowing oil accompanying vaporization in the critical region. Ordinarily, when viewed by transmitted light, the liquid colour was yellowish, changing to a yellowish-grey fog as the pressure was lowered. In the critical region, however, the appearance of this fog was accompanied by a very distinct red colour just before it completely filled the tube. This red colour was unmistakable and occurred for every oil examined. In the case of narrow-boiling stocks it was visible over a temperature range of 1° or 2° F., while for some blended stocks having a wide boiling range it was visible over a 10° F. temperature range. The middle of this range was taken to be the critical temperature. The upper and lower boundaries were quite sharply defined in every instance.

This identification of the critical point with the red colour change is in close accord with a similar phenomenon observed when using the static method. The vanishing of the meniscus is always accompanied by a fog or mist formation showing colour change. This phenomenon of light scattering is called "critical opalescence," and has been taken as an indicator of the critical point by some observers, although others claim that critical temperatures measured in this way differ by a fraction of a degree from those obtained by observing the disappearance of the meniscus. Even if this difference exists, the resulting error is much smaller than the other experimental errors.*

Since petroleum fractions are mixtures of pure substances, they therefore possess, in addition to a critical point, a point of maximum temperature and a point of maximum pressure. In order to eliminate any doubt as to which of these three points is being measured by the flow method, this phase of the investigation merits detailed treatment. The border curves shown on Fig. 2 will illustrate the question at issue. A border curve is the locus of the points in the pressure–temperature plane which separate the homogeneous state (liquid or vapour alone) from the heterogeneous state (liquid and vapour together). On Fig. 2 the boiling curve, *i.e.* the locus of points at which the first vapour trace appears, or the last disappears, is represented by a solid line. The dew curve, or locus of points at which the first trace of liquid appears, or the last trace disappears, is represented by a broken line. These two curves meet in the critical point C. P is the point of maximum pressure, while T is the point of maximum temperature. In general, P and T do not coincide with C except for pure compounds.

* Note added in proof : The recent development of the large-size Polaroid polarizing screens makes it probable that other methods of determining the critical point can be developed, based on the depolarization of scattered light. Work is now being undertaken along this line.

An examination of the border curve without regard to the type of phenomena which identify the critical point C could give rise to the suspicion that either the point of maximum pressure P, or the point of maximum temperature T, since these are outstanding points, is being mistakenly identified with the critical point. Definite experimental evidence was obtained that the critical point was observed, and not the point of maximum pressure or maximum temperature, since it was found possible to follow the border curve of wide boiling blends in the critical region. While for wide boiling blends the difference between the maximum pressure and the critical pressure never exceeded 10 lb. per square inch, the point of maximum temperature differed from the critical point by as much as 50° F., and 200 lb. per square inch.

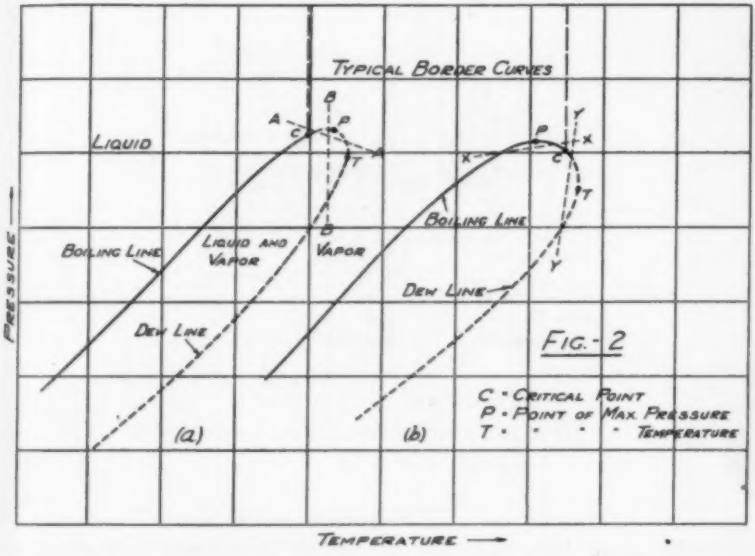


FIG. 2

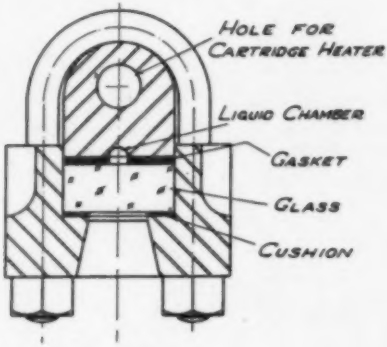
The validity of the results obtained by the flow method has been confirmed also by comparison with those obtained by the static method, when the type of stock permitted. For example: The critical temperature of a Mid-Continent kerosine was found to be 759° F. by a static method and 758° F. by the flow method.

APPARATUS.

As a result of the preliminary work mentioned above, an apparatus capable of handling gas oils was constructed, the main features of which were as follows: The oil under pressure from a nitrogen cylinder was first heated to 750° F. in several coils immersed in lead baths and then rapidly raised to its critical temperature in another lead bath containing 15 feet of 0·072-inch I.D. steel tubing. Observation of the critical phenomena

was made in a special quartz chamber inserted at this point, after which the oil was cooled to room temperature in a water-bath and the flow rate measured.

Observation Chamber—Early Designs. It was clear from the beginning that the only difficult problem lay in the design of the observation chamber. The first one tried was a modified Jerguson gauge glass of the reflecting type, but with a non-corrugated window. Fig. 3 shows a section through the modified gauge. It was not possible to use the transparent type gauge glass because of the unavoidably large liquid chamber required. It was found that the ordinary type of so-called "high-temperature" gasket was a complete failure. A monel metal–asbestos gasket was tried, but was unsuccessful because the gasket slot was too small to allow sufficient overlapping of the monel metal sheath. A mica gasket gave fair results



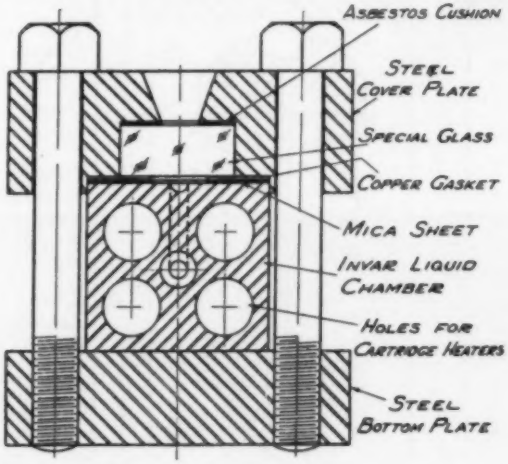
SECTION OF
JERGUSON REFLEX
GAGE GLASS
FIG.-3

with this type of observation chamber, but the design proved unsatisfactory, chiefly because of the strain on the glass necessary to make the gasket tight at high temperatures.

A second observation chamber was then built following the design of the "loose-window" gauge glass.[9] In this type the pressure joint is made between two metal surfaces, leaving the glass, which is separated from the oil by a continuous sheet of mica, free to adjust itself under the internal oil pressure only. Details of the design are clearly shown by Fig. 4. This observation chamber was found to be pressure tight, but suffered from two other defects, one of which was the dehydration and consequent darkening of the mica window at high temperatures, and the other was the rapid coking of the invar backing, which made observation difficult. The latter defect can be overcome to some extent by use of a glazed porcelain slip in the invar slot. Both defects made it necessary to take the chamber apart for cleaning after every run. There is little

doubt that this chamber could have been used, with difficulty, up to about 920° F., but the advantage offered by another design caused its abandonment.

Observation Chamber—Final Design. The final form of observation chamber is shown by Fig. 5. A fused quartz cylinder 3½ inches long, 2 inches in diameter, and having an axial hole 5 mm. in diameter is held between the invar ends of a self-aligning compression yoke using ball-cone seats, the quartz-invar joints being gasketed with copper-asbestos rings (spark plug type). The ends of the quartz were highly polished and coated with powdered graphite to allow mutual slipping of the gasket and the quartz, eliminating shearing stresses. Invar end-pieces were used to minimize relative expansion between them and the quartz.



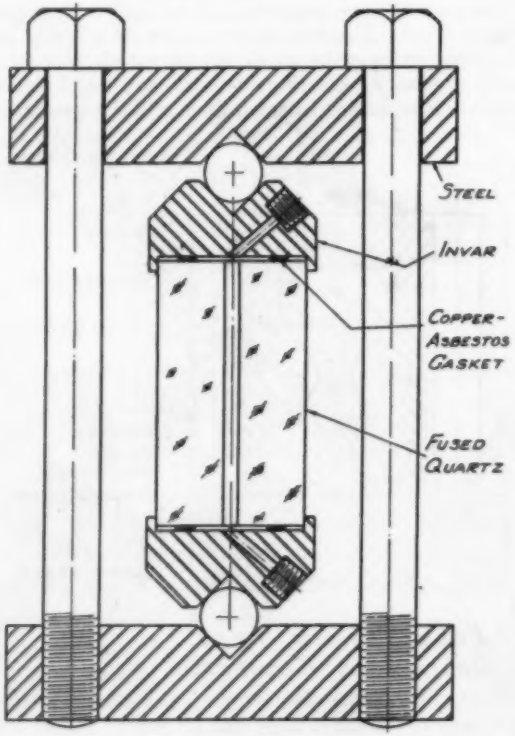
LOOSE WINDOW TYPE OBSERVATION CHAMBER
FIG.-4

Heat loss from the oil flowing through the quartz was reduced by a helical nichrome heating coil threaded through mica spacers fastened to aluminium posts separating two transite rings.

Cleaning of Observation Chamber. While it was found an easy matter to burn out any coke deposition on the inside of the quartz cylinder, the deposition of iron oxide which results from burning out the steel tubing made it necessary to dismantle the chamber and to clean it after every three to five runs. This is a very simple task, since what iron oxide cannot be simply swabbed out is readily dissolved in hydrochloric acid without injury to the quartz.

Fractures in Quartz. During the course of the measurements the fused quartz cylinder developed a number of incipient conchoidal fractures extending from each end diagonally outwards into the quartz. One of

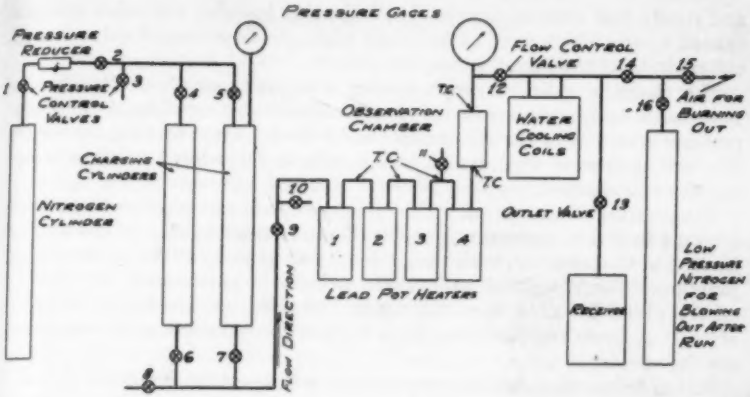
these is about one-half inch long. These incipient fractures originated under the copper–asbestos gaskets, and seem to have first appeared when the gaskets were quite flat, without much yield. For some time it was feared that the quartz would break, but the use of new and yielding gaskets has prevented increase in the size and number of the incipient fractures. To prevent these fractures a frequent renewal of the gaskets is desirable.



QUARTZ OBSERVATION CHAMBER
FIG. 5

Experimental. The complete apparatus can be visualized by reference to the flow diagram Fig. 6 and the photograph Fig. 7. The flow diagram is self-explanatory. The valve numbers on the flow diagram and the photograph are identical.

Four lead-immersed heating coils supply the heating capacity necessary when flow rates of 35,000–50,000 ml. per hour are used to prevent cracking of the oils having critical temperatures above 950° F. An important feature of the apparatus is the location of the forged steel flow control valve, 12, between the observation chamber and the cooling system. The presence of this valve in the hot oil line has made possible accurate



FLOW DIAGRAM FOR CONTINUOUS FLOW CRITICAL CONSTANT APPARATUS

FIG - 6

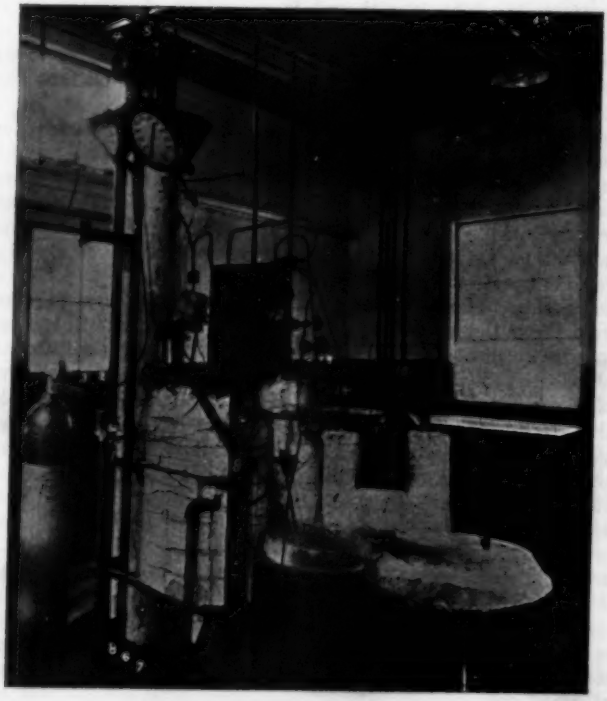


FIG. 7.

and steady flow control, completely eliminating foaming and other troubles caused by gas which were experienced when the flow control valve was in the position of the outlet valve, 13.

The charging cylinders, each having a capacity of about 10,000 ml., were made long and narrow to prevent appreciable solution of the high-pressure nitrogen in the oil during the 15–30 minutes required for a run. The cylinders were wound with steam coils and insulated to allow waxy stocks to be charged.

Temperature Measurement. The oil temperature was measured by means of two $\frac{1}{8}$-inch iron–constantan pencil thermocouples welded in the tubing leading to the chamber, with their tips almost exposed at the invar–quartz junction. The shank of each thermocouple is surrounded by flowing oil for about 3 inches from the tip to the weld, minimizing conduction errors. A Leeds and Northrup Type K Potentiometer was used to measure the thermocouple e.m.f.

It was found that at high temperatures a temperature gradient of 5–10° F. existed along the observation chamber despite the action of the heating coil mentioned above. It is believed that this gradient was due to heat losses from the upper invar end-piece, which cannot be readily insulated in the present design. Whenever this gradient existed an average of the two temperatures was taken. It is not believed that an appreciable error was introduced by it, although it should be eliminated by better design.

Pressure Measurement. The oil pressure was measured by means of a 1000 lb. per square inch gauge equipped with a 10-inch dial calibrated in intervals of 10 lb.

Calibration. Before starting the final group of seventy odd runs, the top pencil thermocouple and the pressure gauge were recalibrated. The thermocouple calibration was found to be unchanged when compared with a standard platinum–platinum 10 per cent. rhodium thermocouple. The pressure gauge was found to read 5 lb. per square inch too high, so that only 10 lb. instead of 15 lb. were added to the observed gauge pressure to convert to absolute pressure.

Contact Times. The flow rates were measured by observing the amount of oil from the outlet valve, 13, which ran into a graduate in ten seconds. An approximate idea of the time of contact at the highest flow rate can be obtained from the following figures for the cold contact times for various parts of the apparatus. The last preheater coil has 12 feet of 0·216-inch I.D. tubing, while the capillary heating coil has 15 feet of 0·072-inch I.D. tubing. Using these figures, and assuming a flow rate of 45,000 ml. per hour, the following cold contact times can be calculated :

1. In last preheater	6·91	seconds
2. In capillary heating coil	0·960	,,
3. In quartz chamber	0·14	,,
4. In tubing containing thermocouples, one end only	0·233	,,

From the values for the critical densities of pure hydrocarbons one can estimate a hot contact time of from one-half to one-third of the above figures.

Observational Procedure.

A brief description of the procedure may be of interest. For high-temperature runs three observers were necessary—one to read the flow rate, one to operate the potentiometer which measured the two thermocouple e.m.f.'s and one to observe the critical phenomena and control the pressure and temperature accordingly. For oils not exceeding 850° F. in critical temperature the flow rate could be estimated sufficiently well by the eye, eliminating one observer.

The lead baths were first brought up to temperature, which, of course, varied with the oil charged. For critical temperatures below 750–800° F. the first two baths were not used. For higher critical temperatures the outlet temperature of bath 3 was adjusted to lie in the range 750–800° F., the temperatures of baths 1 and 2 being adjusted to give about a 250° F. increase per bath. The temperature of bath 4 was adjusted to be slightly over the expected critical temperature, except in the case of high temperatures, when bath 4 was limited to 900° F. at the start of the run.

With valve 9 closed, the nitrogen pressure on the charging cylinders was raised to 200 lb., valve 9 opened, and valve 12 adjusted to give the desired flow rate. The nitrogen pressure was then raised until the flowing oil was in the liquid state in the observation chamber and the oil temperature gradually raised to the critical point by increasing the temperature of bath 4. During observation the pressure gauge was constantly tapped to eliminate sticking. It was found most convenient to raise the pressure above the critical, and then to read pressure and temperature simultaneously as the pressure slowly fell through the critical region. The general idea of the observations may be described as a super-position of a fairly rapid pressure variation up and down through the critical region upon a slow temperature rise and fall in this region. The top thermocouple was read first, followed as rapidly as possible by the bottom couple. The temperature interval between the two couples was kept below 10° F. by controlling the current in the heating coil surrounding the quartz chamber, and was generally considerably less.

Effect of Cracking.

From runs at high temperature and medium flow rates it was found that the amount of cracking had a pronounced effect on increasing the observed critical pressure. Therefore, this effect was used to determine whether cracking was occurring at any given flow rate, by observing whether any fall in critical pressure followed a considerable increase in flow rate. If no fall or other change occurred, it was assumed that the effect of cracking was entirely negligible. We can safely say that the critical temperatures measured were not appreciably affected by any cracking up to the highest values measured, but the critical pressures of the high critical temperature oils are somewhat uncertain, since for these it was not possible to further increase the flow rate and at the same time maintain the temperature.

In Appendix II are listed a few typical data sheets showing the difference between the maximum temperature, maximum pressure, and critical

point, as well as the spread of the critical region in temperature as indicated by the red colour change. Also, the effect of varying the flow rate on the observed critical pressure of a stock having a high critical temperature is shown.

Range of Fractions Measured.

Critical temperature and pressure data have been obtained on over one hundred petroleum fractions. The critical temperatures measured range from 550° to 1000° F., and the critical pressures from 250 lb. to 700 lb. per square inch absolute. Most of these fractions were made up by blending eight base stocks, viz. :—

1. Mid-Continent Straight-Run Gasoline.
2. Naphthene Base Straight-Run Gasoline.
3. Cracked Naphtha.
4. Mid-Continent Kerosine.
5. Mid-Continent Gas Oil.
6. Naphthene Base Gas Oil.
7. No. 1 Cycle Gas Oil.
8. No. 2 Cycle Gas Oil.

In addition, data were obtained on various gas oils from naphthene base, Mid-Continent, and Pennsylvania crudes, as well as blends of a solvent-refined SAE-20 motor oil with kerosine.

Measurements on stocks containing gas and on the products from cracked gas oils have been deferred to the future because the present equipment is not capable of charging these stocks. Limitations of the present apparatus also prevented the measurement of stocks having critical temperatures higher than 1000° F. A complete tabulation of the experimental results is given in Appendix I, together with specific gravity and distillation data on all stocks.

Critical Temperature of Mixtures of Fractions.

Figs. 8 to 10 show the critical temperature of various two-fraction blends, plotted against volume per cent. of the heavier fraction. It will be observed that on most graphs the critical temperature deviates slightly from a linear function of volume per cent., being convex upward. On Fig. 8 the critical temperature is plotted against weight per cent., which gives a more nearly linear relationship, and against mol per cent., which gives a much greater deviation from linearity.

Critical Temperature Correlation.

Using the data from this investigation, as well as the data for the eleven pure hydrocarbons shown in Appendix I, a correlation of critical temperature with specific gravity 60/60° F., and volumetric average boiling point (V.A.B.P.), was developed. The V.A.B.P. is defined here as the arithmetic mean of the temperatures at the 10, 30, 50, 70, and 90 per cent. points of an A.S.T.M. distillation.

It was made clear during the course of this investigation that only the

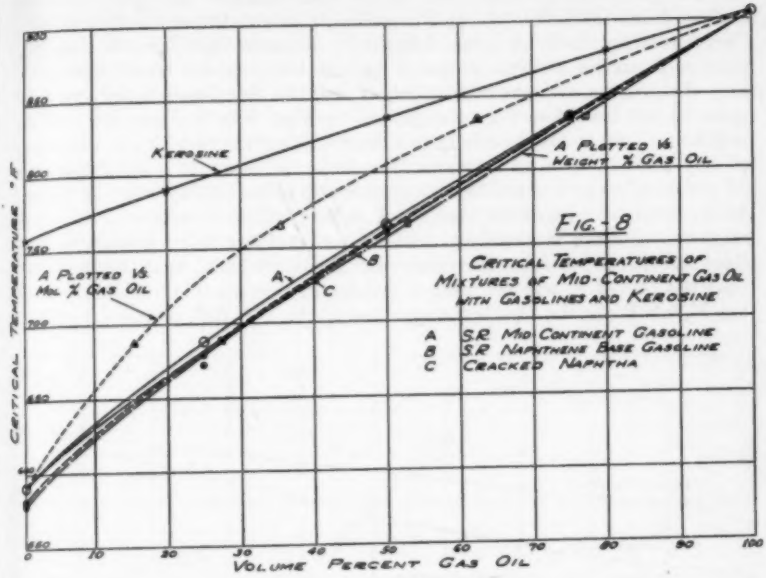


FIG. - 8

CRITICAL TEMPERATURES OF MIXTURES OF MID-CONTINENT GAS OIL WITH GASOLINES AND KEROSINE

A S.R. MID CONTINENT GASOLINE
B S.R. NAPHTHENE BASE GASOLINE
C CRACKED NAPHTHA

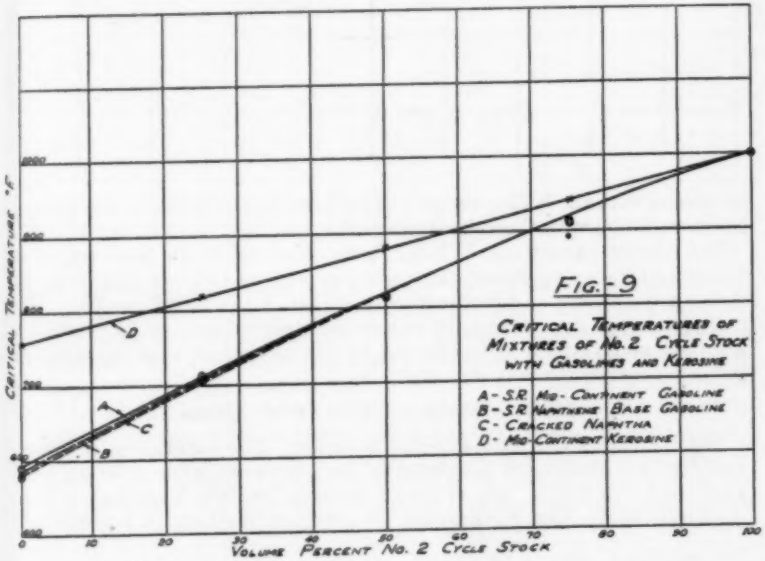


FIG. - 9

CRITICAL TEMPERATURES OF MIXTURES OF No. 2 CYCLE STOCK WITH GASOLINES AND KEROSINE

A - S.R. MID-CONTINENT GASOLINE
B - S.R. NAPHTHENE BASE GASOLINE
C - CRACKED NAPHTHA
D - MID-CONTINENT KEROSINE

V.A.B.P., and not the A.S.T.M. 50 per cent. point or the molal average boiling point (M.A.B.P.) [8] could possibly fit the data on blended stocks. The reasoning involved is the following: Suppose that for non-blended, relatively narrow boiling stocks a critical temperature correlation with any of the three average boiling points could be developed, as is probably true. Then consider, from the curves on Figs. 8 to 10, how the blends will fit in. Since the blends have a wide boiling range which is not completely filled in with all fractions from light to heavy, it is clear that the 50 per cent. point will not be an approximate mean boiling point for them. It has been found by trial that the V.A.B.P. will form a satisfactory correlation variable, since their critical temperatures vary approximately linearly with the volume per cent. On the other hand, it is equally clear that the M.A.B.P. will not form a satisfactory correlation variable,* since the M.A.B.P. for the blends (being equal to the V.A.B.P. minus a quantity

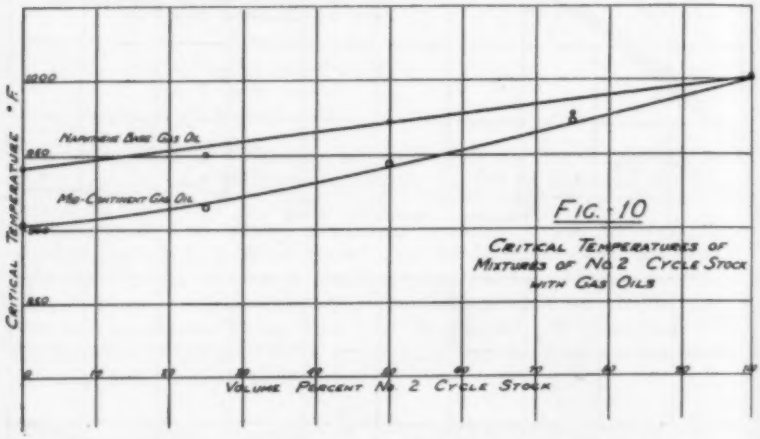


FIG. 10

CRITICAL TEMPERATURES OF MIXTURES OF No 2 CYCLE STOCK WITH GAS OILS

increasing with the boiling range) will fall considerably below the necessary linear variation with the volume per cent.

The specific gravity and V.A.B.P. were combined in the same way that Eaton and Porter combined the specific gravity and 50 per cent. point to define a quantity a = (specific gravity, 60/60° F.) (V.A.B.P. + 100). By fitting a second degree equation in a to the observed data on 95 petroleum fractions and 11 pure hydrocarbons, by the method of least squares, the following correlation was obtained:

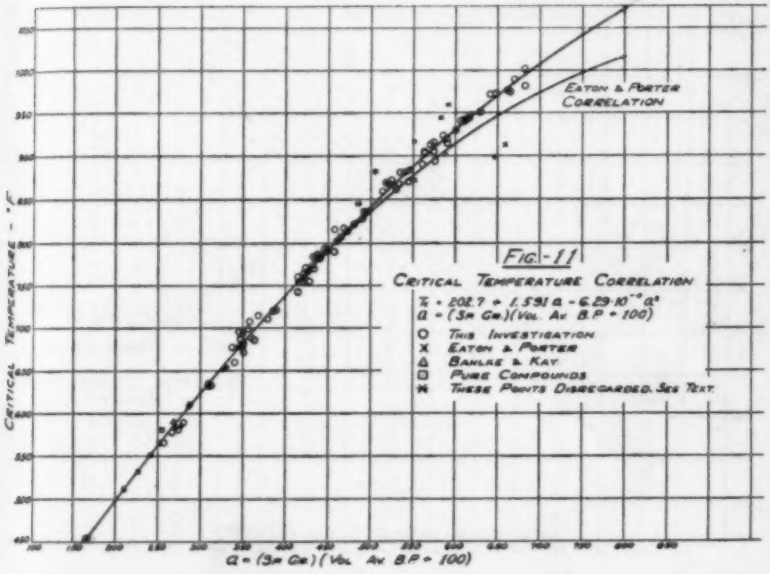
$$T_c = 202{\cdot}7 + 1{\cdot}591a - 6{\cdot}29 \times 10^{-4}a^2 \text{ degrees F.}$$

Fig. 11 shows the data and the equation. The correlation of Eaton and Porter is also shown (assuming for the purpose equality of 50 per cent. point and V.A.B.P.). The deviation between the two is marked at temperatures above 850° F., showing the result of cracking in lowering the

* This applies to blends only. For normal stocks, for which the M.A.B.P. and the V.A.B.P. differ but slightly, either can be used satisfactorily.

critical temperatures determined by the static method. Eaton and Porter's data, as well as two points obtained by Bahlke and Kay,[6] are plotted also. The correlation of Watson and Nelson [8] predicts critical temperatures which are considerably lower than those observed to much the same extent as does that of Eaton and Porter. Furthermore, since it is based on the molal average boiling point, Watson and Nelson's correlation shows even greater discrepancies when applied to the blended fractions.

In forming the correlation certain points, marked by asterisks on Fig. 11, have been omitted for the reasons to follow: Samples 1445, 1447, 1448, and 1446, respectively, mixtures of a Mid-Continent kerosine with 20, 30, 40, and 50 volume per cent. of a solvent refined SAE-20 oil, lie considerably

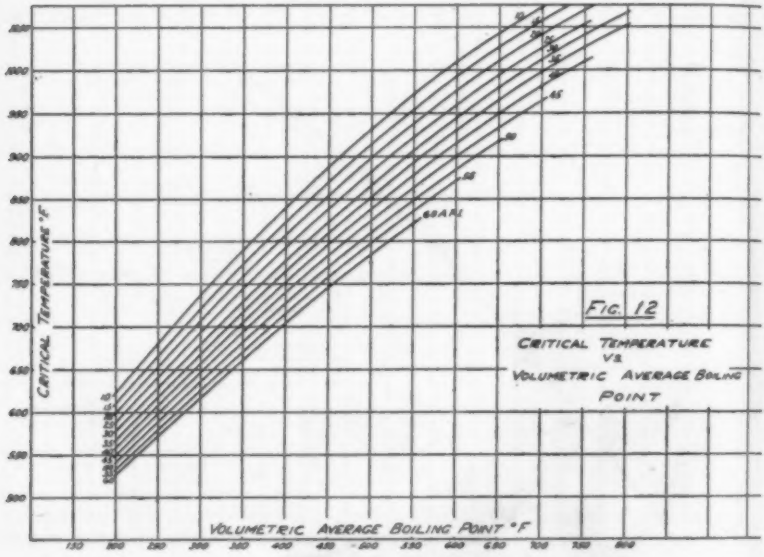

EATON & PORTER CORRELATION
FIG. 11
CRITICAL TEMPERATURE CORRELATION
T_c = 202.7 + 1.591 Q - 6.29·10^-4 Q^2
Q = (Sp. Gr.)(Vol. Av. B.P. + 100)
THIS INVESTIGATION
EATON & PORTER
BAHLKE & KAY
PURE COMPOUNDS
THESE POINTS DISREGARDED. SEE TEXT
CRITICAL TEMPERATURE - °F.
Q = (Sp. Gr.)(Vol. Av. B.P. + 100)

above the correlation curve. Since there was no reason to suspect the critical data, it was thought that the distillation data were too low at the high-temperature end due to cracking. This assumption was confirmed qualitatively by a vacuum distillation (pressure less than 1 mm. Hg) of the heavy oil. The resulting boiling curve at atmospheric pressure was much higher than that found by the A.S.T.M. distillation test. A quantitative check was not possible, because of uncertainty regarding the pressure at which the vacuum distillation was run. The same explanation applies to sample 1415, which was a mixture of 1393 and 1389, which were, respectively, heavy and light distillates from a topped Pennsylvania crude.

The maximum deviation from the calculated curve is 18° F., while the root mean square deviation is 6·5° F. An accepted quantitative way of determining the fit of the above equation to the observed points is to

calculate the probable error of T_c as a function of a. The probable error is, by definition, a number such that the true error is equally likely to be either greater or less than this number. The probable error of a function will be a minimum at a certain point called the "centre of gravity" of the observations, and will increase on each side of this point. Thus, the calculated probable error furnishes a quantitative evaluation of the accuracy of the calculated function, not only in the vicinity of the data, but also in the extrapolated region on either side of the data.

The probable error of the critical temperature correlation has been calculated for two points: $a = 400$ and $a = 600$, corresponding respectively to $T_c = 737°$ F. and $T_c = 933°$ F. The result is plus or minus 0·55° F. at $a = 400$ and plus or minus 0·72° F. at $a = 600$. The calculation


CRITICAL TEMPERATURE °F
VOLUMETRIC AVERAGE BOILING POINT °F
FIG. 12
CRITICAL TEMPERATURE VS. VOLUMETRIC AVERAGE BOILING POINT

is somewhat lengthy, and so it has been made for these two points only, in order to give a general idea of the accuracy of the correlation. It is clear that the difference between the root mean square deviation of 6·5° F. and the probable error of less than 1° F. is due to the large number of observations involved.

A sample calculation of the probable error in a simpler problem is given in Appendix III. This method, while well known, is very clearly described by Birge.[7]

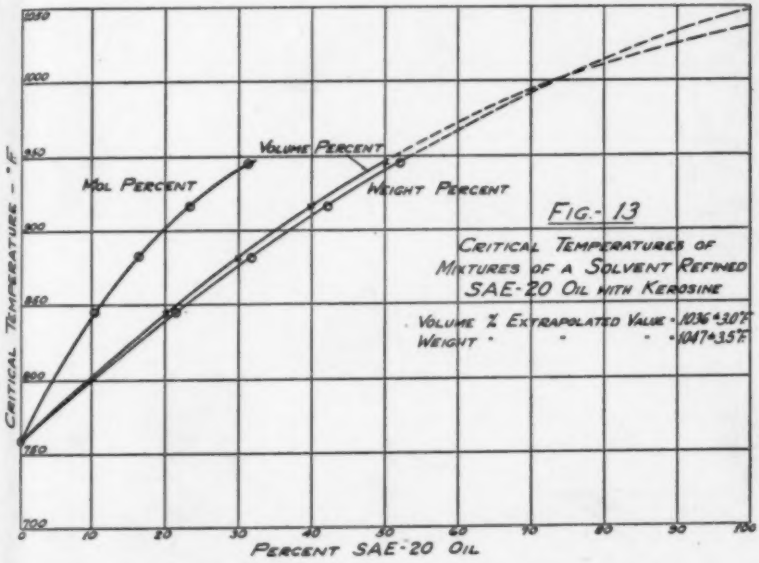
It is not claimed that the absolute accuracy of the measured critical temperatures is as small as 1° F., but an estimated accuracy of plus or minus 4° F. appears justifiable. It seems probable that some of the larger deviations from the correlation curve were caused by a combination of this error in the critical temperature and a similar or greater error in the

volumetric average boiling point, as calculated from the A.S.T.M. distillation. The smoothness of the curves of critical temperature for the two component mixtures, which are, of course, independent of the A.S.T.M. distillation, gives further support to the claimed critical temperature accuracy.

The critical temperature correlation equation is plotted in a more useful form against the V.A.B.P. and the A.P.I. Gravity on Fig. 12.

Critical Temperature of Heavy Fractions by Extrapolation.

An attempt was made to obtain the critical temperature of heavy stocks by determining the critical temperatures of blends with kerosine



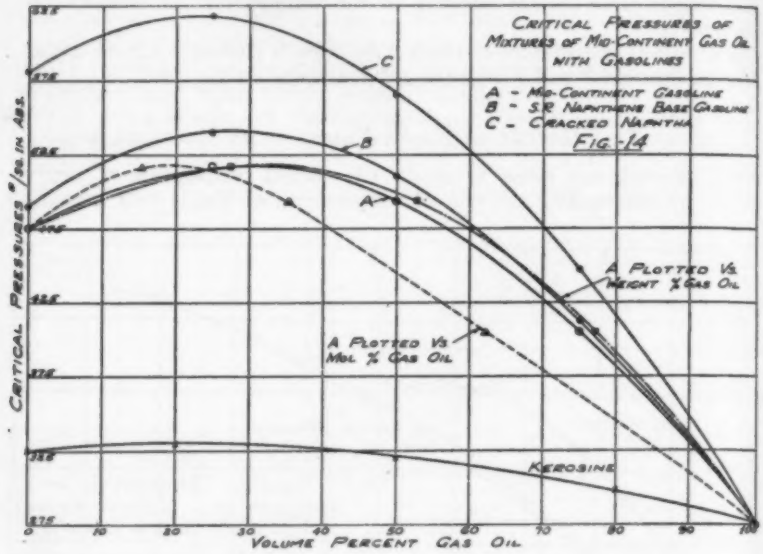
and extrapolating to zero per cent. kerosine. The limitations imposed by insufficient heating capacity and charging volume (obviously by no means insuperable) prevented direct observation of the critical temperature at the high flow rate necessary to prevent cracking.

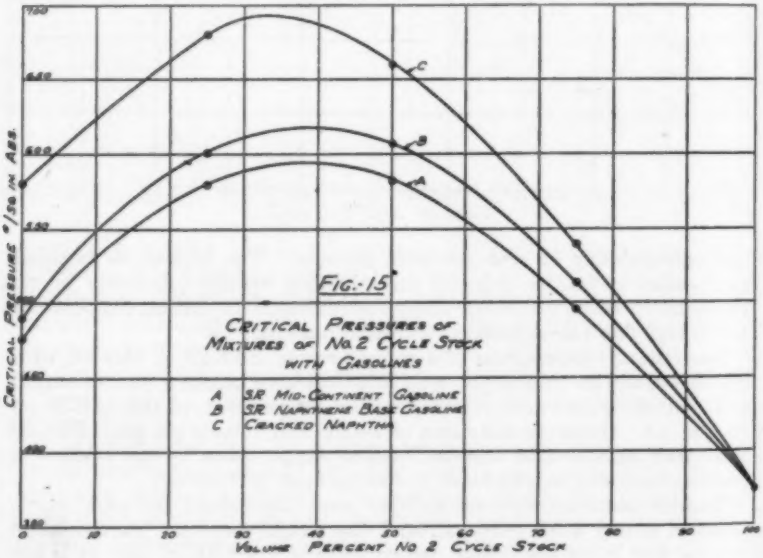
The critical temperatures of a solvent-refined SAE-20 oil blended with 80, 70, 60, and 50 volume per cent. Mid-Continent kerosine were measured and plotted against mol, volume, and weight per cent. of the SAE-20 oil on Fig. 13. Quadratic functions of weight and volume per cent. SAE-20 were then fitted to the observed critical temperatures by the method of least squares, and extrapolated to 100 per cent. SAE-20 oil.

The fits obtained were surprisingly good, the volume per cent. extrapolation giving $1036 \pm 3{\cdot}0°$ F. and the weight per cent. extrapolation $1047 \pm 3{\cdot}5°$ F. as the critical temperature of the SAE-20 oil. It is not

possible to check these figures from the main correlation until accurate distillation data are obtained.

The details of this calculation are given in Appendix III.


CRITICAL PRESSURES OF MIXTURES OF MID-CONTINENT GAS OIL WITH GASOLINES
A - MID-CONTINENT GASOLINE
B - S.R. NAPHTHENE BASE GASOLINE
C - CRACKED NAPHTHA
FIG.-14
CRITICAL PRESSURES #/SQ. IN ABS.
A PLOTTED VS WEIGHT % GAS OIL
A PLOTTED VS MOL % GAS OIL
KEROSINE
VOLUME PERCENT GAS OIL


CRITICAL PRESSURE #/SQ. IN ABS.
FIG.-15
CRITICAL PRESSURES OF MIXTURES OF NO. 2 CYCLE STOCK WITH GASOLINES
A S.R. MID-CONTINENT GASOLINE
B S.R. NAPHTHENE BASE GASOLINE
C CRACKED NAPHTHA
VOLUME PERCENT NO 2 CYCLE STOCK

Critical Pressure of Mixtures of Fractions.

Figs. 14 to 16 show the critical pressure of various two-fraction blends plotted against volume per cent. of the heavier fraction. It will be observed that there is a distinct maximum in these curves, which is sharper and higher the greater the separation between the mean boiling points of the blended fractions. A similar behaviour has been reported in the literature for binary mixtures of many pure compounds.[10]

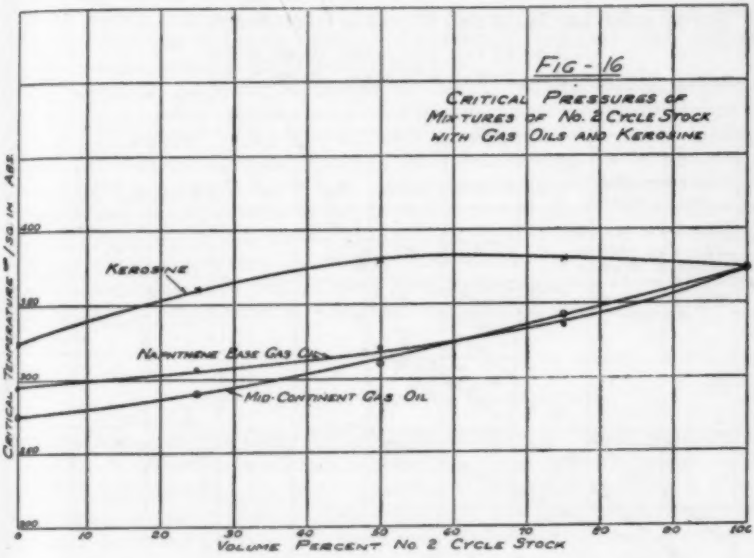


FIG - 16
CRITICAL PRESSURES OF MIXTURES OF No. 2 CYCLE STOCK WITH GAS OILS AND KEROSINE
CRITICAL TEMPERATURE °F / SQ IN ABS
KEROSINE
NAPHTHENE BASE GAS OIL
MID-CONTINENT GAS OIL
VOLUME PERCENT No. 2 CYCLE STOCK

Critical Pressure Correlation.

A correlation between the critical pressure, the critical temperature, the molecular weight, and the slope of the A.S.T.M. distillation curve (defined as 1/80 of the difference between the temperatures at the 90 per cent. and 10 per cent. points) has been established, and is shown plotted on Fig. 17. The form of the correlation is that based on van der Waals' equation.[11] The equation used is

$$P_c = \frac{AT_c}{M}$$

in which

P_c = critical pressure (lb./sq. in. abs.)
T_c = critical temperature (° R.)
M = molecular weight
A = a function of the slope of the A.S.T.M. distillation curve and of the type of fraction.

The following equations for A were developed by fitting straight lines to the data by the least squares method:

For virgin gas oils, kerosine, and Bahlke and Kay's naphtha, a total of 18 measured points:

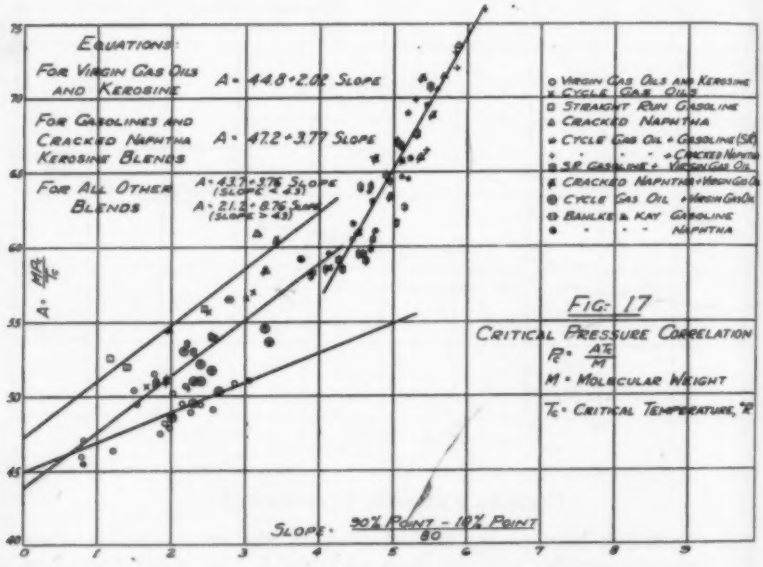
$$A = 44{\cdot}8 + 2{\cdot}02 \text{ slope} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For gasolines, including straight-run, cracked naphtha, kerosine-cracked naphtha blends, and Bahlke and Kay's gasoline (8 points):

$$A = 47{\cdot}2 + 3{\cdot}77 \text{ slope} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For all other blends (24 and 45 points, respectively):

$$A = 43{\cdot}7 + 3{\cdot}76 \text{ slope} \quad \text{Slope} < 4{\cdot}3 \quad . \quad . \quad . \quad (3)$$
$$A = 21{\cdot}2 + 8{\cdot}76 \text{ slope} \quad \text{Slope} > 4{\cdot}3 \quad . \quad . \quad . \quad (4)$$


EQUATIONS:
FOR VIRGIN GAS OILS AND KEROSINE A = 44.8 + 2.02 SLOPE
FOR GASOLINES AND CRACKED NAPHTHA KEROSINE BLENDS A = 47.2 + 3.77 SLOPE
FOR ALL OTHER BLENDS A = 43.7 + 3.76 SLOPE (SLOPE < 4.3)
A = 21.2 + 8.76 SLOPE (SLOPE > 4.3)
VIRGIN GAS OILS AND KEROSINE
CYCLE GAS OILS
STRAIGHT RUN GASOLINE
CRACKED NAPHTHA
CYCLE GAS OIL + GASOLINE (S.R.)
CRACKED NAPHTHA + VIRGIN GAS OIL
CYCLE GAS OIL + VIRGIN GAS OIL
BAHLKE & KAY GASOLINE
NAPHTHA
FIG. 17
CRITICAL PRESSURE CORRELATION
P = AT_c / M
M = MOLECULAR WEIGHT
T_c = CRITICAL TEMPERATURE, °F
SLOPE = 90% POINT − 10% POINT / 80
A = MT_c / P

The following table gives the r.m.s. deviation and probable errors in A at different slopes for the above four equations:

PROBABLE ERROR.

Equation:	(1).		(2).		(3).		(4).	
Slope 0 . .	0·54	1·2%	0·85	1·8%	0·92	2·1%	—	—
„ 1 . .	—	—	0·55	1·1	—	—	—	—
„ 2 . .	0·18	0·37	0·30	0·55	0·34	0·66	—	—
„ 3 . .	0·35	0·69	0·32	0·55	—	—	—	—
„ 4 . .	—	—	0·58	0·93	0·44	0·75	0·49	0·87%
„ 5 . .	—	—	—	—	—	—	0·20	0·31
„ 6 . .	—	—	—	—	—	—	0·48	0·65
R.m.s. deviation .	1·24		0·96		1·60		1·90	

The molecular weights used in calculating A were estimated by the use of Watson and Nelson's correlation.[8] It was found by trial that the molecular weights of blends estimated by this method were in good agreement with the harmonic average molecular weights calculated from those of the individual components.

Certain observed critical pressures were disregarded in developing the correlation. This was done whenever the stock had a high critical temperature and the observation indicated cracking had occurred, as was generally true of such stocks which were run before the heating capacity of the system was increased. The SAE-20 motor oil-kerosine blends were also omitted due to the uncertainty in estimating their molecular weights from the obviously incorrect distillation data.

It would be desirable if a simple correlation between critical pressure and only two other variables, such as slope and some average boiling point, could be developed. This does not seem possible, since the density enters into both the critical temperature and the molecular weight in an important way. For a given V.A.B.P. the critical temperature increases and the molecular weight decreases as the density is increased, so that their ratio is even more sensitive to density change than is either of them. Therefore, if the above correlation be considered significant, the critical pressure must be considered to depend on at least three variables, which makes it impossible to plot it directly. No improvement is obtained if the M.A.B.P. is used.

New Critical Pressure Correlation.

The critical pressure correlation based on Van der Waals' equation is usable only when it is known which of the above equations fits the particular fraction in question. Since the selection of the proper equation is often uncertain, a new critical pressure correlation has been developed which has the following definite advantages over the correlations just described:

1. It uses variables—namely, the A.S.T.M. slope, the M.A.B.P., and the Watson and Nelson characterization factor [8]—which are directly computable from readily measured properties of the fraction, and do not depend upon other correlations which may change with improved data.
2. The new correlation is simpler and easier to apply.
3. The new correlation eliminates the ambiguous specification of type of fraction which was a major defect of the first correlation.
4. The new correlation has been extended to zero slope, *i.e.* to pure compounds. This fact offers considerable support for its fundamental soundness.

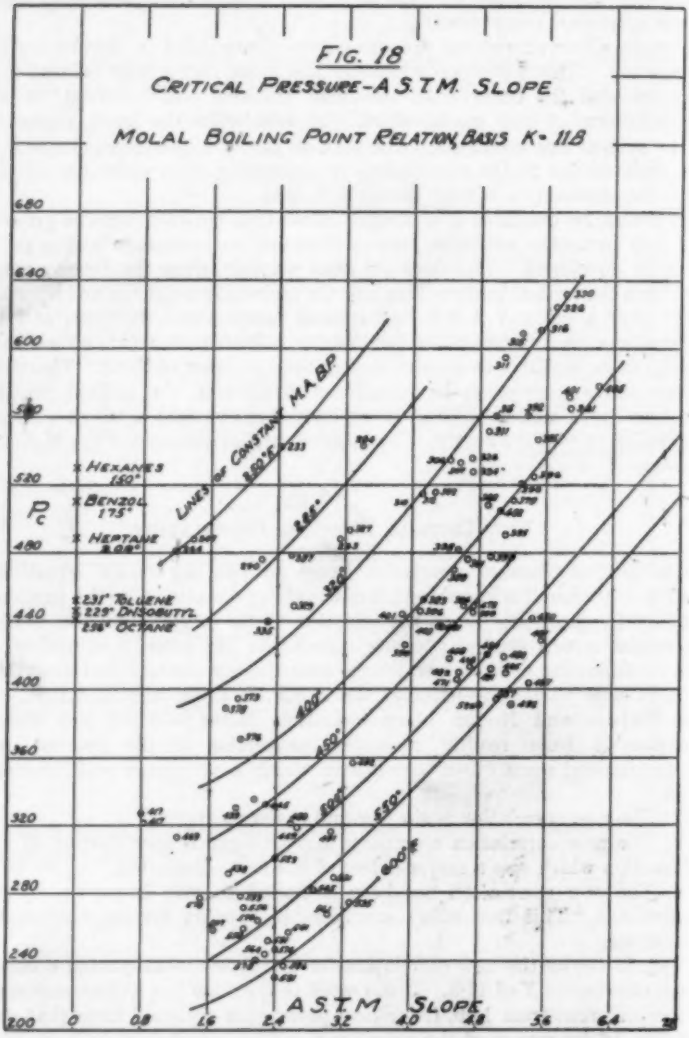
Fig. 18 shows the new correlation for distillate stocks having a characterization factor X of 11·8. If the stock in question has a characterization factor different from 11·8, its critical pressure is obtained from that given by Fig. 18 by means of the equation:

$$P_c \text{ (corrected)} = P_c \text{ (Fig. 18)} - 95\,(X - 11{\cdot}8).$$

The new critical pressure correlation was obtained by eliminating the effect

of one of the above variables at a time, and determining directly the relationship between the remaining ones.

Below is a comparison of the observed critical pressures of five fractions



and those predicted by: (1) the Watson and Nelson [8] method, which is the only published procedure for estimating critical pressures of petroleum fractions; (2) the correlation based on Van der Waals' equation; and (3) the new correlation.

Number:	1419.	1418.	1453.	1454.	1507.
Oil:	Mid-Continent Gas Oil.	Naphthene Base Gas Oil.	Naphthene Base Gasoline.	No. 1 Cycle Gas Oil.	50% N.B. Gasoline + 50% No. 2 Cycle Gas Oil.
T_c, ° F.	903	942	578	941	816
Mol. wt. (W. & N.)	237	241	110	200	146
10% Point	500	517	198	442	227
M.A.B.P.	554	579	247	528	381
P_c obs. (lb./sq. in., abs.)	275	295	490	399	607
P_c calc. (W. & N.)	400	450	500	550	900
P_c calc. (Van der W.)	281	286	495	388	605
P_c calc. (new)	248	277	495	421	635

It will be seen that the Watson and Nelson prediction is entirely unsatisfactory except for the gasoline. The new correlation predicts moderately well, while the Van der Waals' correlation shows excellent agreement, since in these examples no question arises regarding the choice of the equation giving A.

While none of the correlations has been found to be entirely satisfactory in its accuracy of prediction, it is hoped that further consideration of these correlations, when more critical pressure data have been obtained, will lead to more satisfactory methods.

Conclusions.

The conclusions reached from this work are the following:

1. A new and accurate method of measuring the critical temperature and the critical pressure of petroleum fractions has been developed. This method will measure the critical temperature and the critical pressure of stocks having critical temperatures up to 1000° F., while the best previous work was limited to below 850° F. for critical temperature alone, and to below 700–750° F. for both critical temperature and critical pressure.

2. A new visual observation chamber of fused quartz capable of operating under conditions of at least 1000° F. and 600 lb. per square inch has been developed.

3. Correlations of critical temperature and critical pressure with other physical properties more readily measured have been developed which are believed to have considerable value, particularly because of the large amount of data covering an extensive range which has been used.

Problems Requiring Further Investigation.

There are a number of problems connected with critical constants on which the present apparatus is not able to provide information:

1. The determination of critical volume. This problem seems to be a difficult one to solve, since it requires measurement not only of the cold flow rate, but also the flow velocity at the critical point. Certainly a great amount of research would be necessary to solve it.

2. Measurement of the critical temperature and pressure as a function of the extent of cracking. This problem will require quenching immediately

after the oil has passed through the observation chamber, which is not possible without the use of pumps. It is not certain how much effect cracking will have on coking up the observation chamber, but it seems probable that considerable difficulty would be experienced from this cause.

3. Measurement of the critical temperature and pressure of mixtures containing gases. This problem can be attacked quite easily with a relatively simple modification of the present apparatus to allow charging stocks containing gas under pressure.

4. Measurement of critical temperatures higher than 1000° F. This problem can be solved by increasing the flow velocity and the heating capacity. The flow velocity can be increased by using higher flow rates and somewhat smaller capillary tubing in the last lead pot. A considerable increase in heating capacity, particularly of the last lead pot, would be necessary to handle higher flow rates. A desirable but not absolutely necessary change would be a reduction in the inside diameter of the fused quartz cylinder of the observation chamber.

5. The measurement of the critical constants of reduced crudes or oils containing tarry matter. This problem, while falling partly under (4) above, is more difficult because of the probable rapid coking of the observation chamber. It has been found impossible to run dirty stocks having even relatively low critical temperatures (around 900° F.) because of this last effect. It seems probable that this problem can be solved only to the extent that the reduced crudes can be cleaned and the observed results on the clean oil applied to the original material.

Acknowledgment.

This work was performed under the direction of Mr. Walter Claypoole, to whom the author is grateful for much invaluable advice. The author is indebted to Messrs. C. E. Cummings and A. Jamieson for helpful suggestions regarding the construction of the observation chambers.

The new correlation was developed by Mr. J. R. Keith of the Port Arthur Laboratory of The Texas Company.

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APPENDIX I.

TABULATION OF INSPECTION DATA ON ALL STOCKS, TOGETHER WITH THE CORRELATION VARIABLES AND THE OBSERVED CRITICAL CONSTANTS.

Number:	1261.	1262.	1263.	1264.	1265.	1266.	1267.	1278.
Description:	M-C. Gas Oil.	N.B. Gas Oil.	M-C. Kero-sine.	392 Gaso-line.	75% 1264, 25% 1261.	50% 1264, 50% 1261.	25% 1264, 75% 1261.	75% 1263, 25% 1261.
Gravity, A.P.I. °	36·0	28·2	41·0	58·7	50·8	45·1	41·1	41·3
Sp. Gr. 60/60° F.	0·845	0·886	0·820	0·744	0·776	0·801	0·820	0·819
Aniline Pt., ° F.	168	150	—	—	125	141	—	—
Distillation:								
I.B.P., ° F. .	455	492	380	100	116	118	140	372
10% . .	502	524	394	149	178	188	271	400
20 . .	514	540	400	178	208	240	400	410
30 . .	526	554	406	203	240	289	476	418
40 . .	540	567	412	229	266	353	504	427
50 . .	556	583	418	251	300	441	530	439
60 . .	570	602	426	270	339	508	557	453
70 . .	586	625	434	289	402	542	573	460
80 . .	612	652	444	316	516	575	600	500
90 . .	663	702	460	344	586	628	646	572
95 . .	706	—	476	368	654	—	697	647
End Point .	706	744	492	390	666	700	704	666
Recovery, % .	98·0	98·5	98·0	97·5	95·5	92·0	98·5	96·5
Vol.Av.B.Pt. .	567	598	422	247	341	418	499	458
a . . .	564	619	429	258	342	415	491	457
Slope . .	2·02	2·22	0·82	2·44	5·10	5·50	4·69	2·15
Mol.Av.B.Pt. .	555	585	418	233	299	371	462	446
Mol. Wt. . .	240	247	171	107	126	152	188	184
A . . .	50·1	(57·5)?	47·1	55·9	66·7	70·7	64·0	49·0
T_c Obs., ° F. .	905	922	755	566	660	743	827	790
P_c Obs., lb./in.², Abs. . .	285	(322)?	335	535	593	560	437	333
T_c Deviation from Curve .	+5	−25	−14	−5	−13	−12	−5	−8

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

M-C. = Mid-Continent.

N.B. = Naphthene Base.

Number:	1281.	1282.	1283.	1290.	1384.	1389.	1390.	1391.	1392.
Description:	Topped M-C. Crude.			Second Cycle Stock.	Cuts 1 & 2 plus 9 & 10 M-C. Crude.	Topped Pennsylvania Crude.			
	Cuts 1 & 2.	Cuts 3 & 4.	Cuts 5 & 6.			Cuts 1 & 2.	Cuts 3 & 4.	Cuts 5 & 6.	Cuts 7 & 8.
Gravity, A.P.I. °	35·8	33·1	29·9	23·9	29·2	43·5	40·4	37·0	34·0
Sp. Gr. 60/60° F.	0·846	0·860	0·877	0·911	0·881	0·809	0·824	0·840	0·855
Aniline Pt., ° F.	—	165	175	79	178	167	179	192	204
Distillation:									
I.B.P., ° F.	398	493	586	408	444	382	456	534	594
10%	485	538	608	460	506	418	488	566	646
20	500	549	620	474	530	430	499	578	662
30	512	557	632	488	560	442	511	590	671
40	521	566	642	497	602	453	523	603	681
50	531	577	655	506	670	466	538	617	693
60	543	588	667	521	734	478	552	632	705
70	557	602	684	537	748	496	571	649	719
80	576	624	705	559	760 (78)	519	594	672	733
90	608	659	744	593	—	556	635	708	760 (88)
95	641	703	760 (93)	640	—	597	678	742	—
End Point	657	708	—	654	—	626	684	744	—
Recovery, %	98·5	98·0	—	98·0	—	98·5	98·5	97·5	—
Vol.Av.B.Pt.	539	587	665	517	655	476	549	616	699
a	541	591	671	562	665	466	534	601	683
Slope	1·54	1·51	1·70	1·66	3·55	1·23	1·84	1·77	1·49
Mol. Av.B.Pt.	530	579	655	508	631	469	539	606	691
Mol. Wt.	225	249	300	196	291	199	236	278	(350)?
A	49·5	50·4	(61·9)?	50·7	(72)?	46·4	47·5	51·5	(76·5)?
T_c Obs., ° F.	881	920	990	890	975	807	868	930	982
P_c Obs., lb./in.², Abs.	295	279	(299)?	350	(355)?	295	267	257	(315)?
T_c Deviation from Curve	+2	−3	+3	−8	−8	−1	−5	−2	−12

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

M-C. = Mid-Continent.

Number:	1393.	1410.	1415.	1414.	1418.	1419.	1429.	1430.
Description:	Cuts 9, 10 & 11 Penna Crude.	Cuts 7, 8, 9 & 10 M-C. Crude.	Cuts 1, 2, 9, 10 & 11 Penna Crude.	Topped Penna Crude.	N.B. Gas Oil.	M-C. Gas Oil.	50% 1420 plus 50% 1419.	50% 1420 plus 50% 1418.
Gravity, A.P.I. °	30·4	24·0	36·9	36·9	28·5	35·3	39·1	35·5
Sp. Gr. 60/60° F.	0·874	0·910	0·840	0·840	0·884	0·848	0·829	0·847
Aniline Pt., ° F.	217	205	191	190	149	167	157	146
Distillation:								
I.B.P., ° F.	485	350	295	430	484	446	372	362
10%	670	685	435	482	517	500	412	412
20	700	720	455	517	534	512	426	424
30	725	735	485	554	549	524	440	440
40	740	740	535	590	564	540	456	456
50	750	745	610	627	580	554	476	480
60	755	—	700	667	596	568	500	510
70	760	—	730	710	621	589	528	552
80	765	—	745	742	650	615	565	596
90	770	—	765	760 (87)	692	658	618	656
95	—	—	770	—	732	700	664	710
End Point	—	—	770	—	732	700	674	710
Recovery, %	—	—	98·0	—	98·5	98·0	98·5	98·0
Vol.Av.B.Pt.	—	—	(605)?	628	592	565	495	508
a	—	—	(592)?	611	612	564	494	515
Slope	—	—	3·75	3·54	2·19	1·98	2·58	3·05
Mol.Av.B.Pt.	—	—	579	604	579	554	480	489
Mol. Wt.	—	—	258	276	241	237	199	201
A	—	—	(66·0)?	(60·2)?	50·7	47·8	49·1	51·0
T_c Obs., ° F.	(1005)?	(1007)?	960	940	942	903	837	859
P_c Obs., lb./in.², Abs.	(505)?	(430)?	(363)?	(305)?	295	275	320	334
T_c Deviation from Curve	—	—	+36	0	+1	+3	+2	+4

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

M-C. = Mid-Continent.

N.B. = Naphthene Base.

Number:	1436.	1437.	1438.	1439.	1420.	1445.	1446.	1447.	1448.
Description:	20% 1420 plus 80% 1419.	80% 1420 plus 20% 1419.	20% 1420 plus 80% 1418.	80% 1420 plus 20% 1418.	M-C. Kerosine.	80% 1420 plus 20% SAE −20.	50% 1420 plus 50% SAE −20.	70% 1420 plus 30% SAE −20.	60% 1420 plus 40% SAE −20.
Gravity, A.P.I. °.	36·9	41·6	31·2	40·1	43·3	39·9	35·2	38·4	36·8
Sp. Gr. 60/60° F..	0·840	0·817	0·870	0·825	0·810	0·826	0·849	0·833	0·841
Aniline Pt., ° F. .	163	150	148	146	146	161	180	168	174
Distillation:									
I.B.P., ° F. .	396	366	410	374	378	370	366	368	366
10% . .	450	397	456	398	394	392	399	393	394
20 . .	470	405	478	406	400	400	411	403	403
30 . .	489	413	504	414	406	408	426	413	414
40 . .	510	423	528	423	412	416	452	423	430
50 . .	532	432	556	434	418	426	554	436	456
60 . .	550	444	578	446	424	437	730	456	540
70 . .	574	460	603	465	432	459	750	540	728
80 . .	600	486	634	496	443	554	760 (78)	734	750
90 . .	642	550	684	580	458	756	—	758	760 (86)
95 . .	684	618	730	660	471	760 (92)	—	760 (91)	—
End Point .	697	634	730	682	488	—	—	—	—
Recovery, % .	98·5	98·5	98·0	98·5	98·5	—	—	—	—
Vol.Av.B.Pt. .	537	450	561	458	422	488	586	508	554
a . . .	535	449	575	460	423	485	582	506	551
Slope . .	2·40	1·92	2·85	2·28	0·80	4·55	5·01	4·56	4·82
Mol.Av.B.Pt. .	523	439	543	445	417	453	545	473	516
Mol. Wt. . .	222	182	224	182	172	—	—	—	—
A . . .	49·4	48·1	50·8	48·9	45·9	—	—	—	—
T_c Obs., ° F. .	881	790	905	802	758	844	945	882	916
P_c Obs., lb./in.², Abs. . .	298	330	309	339	325	378	390	383	388
T_c Deviation from Curve . .	+7	0	−5	+1	−5	+18	+29	+35	+27

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

M-C. = Mid-Continent.

Number:	1423.	1424.	1425.	1426.	1427.	1428.	1452.	1453.
Description:	75% 1421 plus 25% 1419.	50% 1421 plus 50% 1419.	25% 1421 plus 75% 1419.	75% 1421 plus 25% 1418.	50% 1421 plus 50% 1418.	25% 1421 plus 75% 1418.	S.-Run Mid-Continent Gasoline.	S.-Run Naphthene Base Gasoline.
Gravity, A.P.I. °	49·2	44·3	39·7	46·8	40·1	33·9	55·4	55·6
Sp. Gr. 60/60° F.	0·783	0·805	0·827	0·794	0·825	0·856	0·757	0·756
Aniline Pt., ° F.	113	133	151	106	121	136	122	128
Distillation:								
I.B.P., ° F.	96	114	132	106	115	120	118	118
10%	156	194	266	168	188	252	222	198
20	198	249	400	186	246	392	242	221
30	242	314	477	245	312	478	252	234
40	281	387	506	285	383	524	262	245
50	322	450	531	326	456	550	273	255
60	371	504	552	376	522	575	283	266
70	428	540	574	436	564	600	293	277
80	500	576	600	528	600	630	303	291
90	598	624	645	624	658	680	317	310
95	—	678	697	—	—	—	330	327
End Point	650	683	704	680	712	724	350	366
Recovery, %	96·0	97·5	98·0	96·5	97·0	97·5	97·5	98·0
Vol.Av.B.Pt.	349	424	499	360	436	512	271	255
a	352	422	496	365	442	524	281	268
Slope	5·52	5·38	4·74	5·70	5·87	5·35	1·19	1·40
Mol.Av.B.Pt.	301	378	462	309	383	467	265	247
Mol. Wt.	126	154	190	128	153	186	116	110
A	68·9	71·3	65·7	71·6	73·5	65·9	52·6	52·0
T_s Obs., ° F.	672	761	836	686	785	867	590	578
P_s Obs., lb./in.², Abs.	618	565	447	641	597	470	476	490
T_s Deviation from Curve	−13	−1	−1	−14	+2	+3	−10	−6

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_s}{T_s}.$$

Number : Description :	1421. Cracked Naphtha.	1461. 25% 1452 plus 75% 1420.	1462. 50% 1452 plus 50% 1420.	1463. 75% 1452 plus 25% 1420.	1464. 25% 1453 plus 75% 1420.	1465. 50% 1453 plus 50% 1420.	1466. 75% 1453 plus 25% 1420.	1467. 25% 1421 plus 75% 1420.	1468. 50% 1421 plus 50% 1420.
Gravity, A.P.I. °	55·3	46·1	49·1	52·7	46·2	49·1	52·1	45·7	48·8
Sp. Gr. 60/60° F.	0·758	0·797	0·784	0·768	0·796	0·784	0·771	0·799	0·785
Aniline Pt., ° F.	90	140	126	134	142	137	133	134	120
Distillation :									
I.B.P., ° F.	92	178	140	127	166	143	127	127	106
10%	137	309	255	229	293	235	215	292	185
20	170	341	282	248	335	266	236	346	260
30	203	363	304	263	362	290	253	378	317
40	236	380	324	278	383	319	268	391	354
50	266	396	346	291	398	351	287	401	377
60	293	408	374	306	409	378	305	410	393
70	323	421	396	324	421	401	334	421	407
80	354	434	417	350	432	420	373	433	423
90	388	452	438	406	448	443	420	450	446
95	418	464	454	442	462	465	446	467	463
End Point	432	482	473	463	480	472	463	482	476
Recovery, %	97·0	98·5	98·5	98·0	98·5	97·0	98·0	98·5	97·5
Vol.Av.B.Pt.	263	388	348	303	384	344	302	388	346
a	275	389	351	310	386	348	310	390	350
Slope	3·14	1·79	2·29	2·21	1·94	2·60	2·56	1·98	3·26
Mol.Av.B.Pt.	243	378	334	290	373	328	286	377	324
Mol. Wt.	109	155	138	124	153	136	123	154	134
A	60·9	50·8	53·0	53·5	51·1	53·9	54·1	54·5	58·6
T_c Obs., ° F.	582	722	682	632	720	679	635	721	678
P_c Obs., lb./in.², Abs.	481	387	438	470	394	451	481	418	497
T_c Deviation from Curve	−11	−4	−2	−3	−3	−1	0	−7	−4

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

Number:	1469.	1470.	1471.	1472.	1473.	1474.	1475.	1476.
Description:	75% 1421 plus 25% 1420.	75% 1452 plus 25% 1419.	50% 1452 plus 50% 1419.	25% 1452 plus 75% 1419.	75% 1453 plus 25% 1419.	50% 1453 plus 50% 1419.	25% 1453 plus 75% 1419.	75% 1452 plus 25% 1418.
Gravity, A.P.I. °	51·8	49·6	44·5	39·8	49·8	44·6	39·8	47·4
Sp. Gr. 60/60° F.	0·772	0·781	0·804	0·826	0·781	0·804	0·826	0·791
Aniline Pt., ° F.	106	134	145	156	138	149	158	127
Distillation:								
I.B.P., ° F. .	98	146	166	190	112	150	178	144
10% . .	153	236	254	280	211	229	265	232
20 . .	196	256	276	346	232	254	347	252
30 . .	240	269	298	457	249	280	466	266
40 . .	283	281	333	507	264	321	512	278
50 . .	321	295	408	532	280	412	533	292
60 . .	352	315	506	552	301	508	548	312
70 . .	378	353	542	572	349	542	570	354
80 . .	401	508	573	602	508	574	602	534
90 . .	427	578	618	643	576	621	640	610
95 . .	453	635	670	688	634	675	684	678
End Point .	463	657	684	697	650	688	696	678
Recovery, % .	97·0	97·5	98·0	98·0	97·5	98·0	98·0	97·5
Vol.Av.B.Pt. .	304	346	424	497	333	417	495	351
a . . .	313	348	422	494	338	415	492	357
Slope . .	3·42	4·27	4·55	4·54	4·56	4·90	4·69	4·72
Mol.Av.B.Pt. .	281	314	389	462	298	378	458	314
Mol. Wt. . .	120	131	159	190	125	155	188	129
A . . .	60·5	59·1	64·0	59·5	59·4	64·9	59·8	60·4
T_s Obs., ° F. .	633	688	764	836	678	760	836	699
P_s Obs., lb./in.², Abs. . .	551	517	493	405	540	510	412	542
T_s Deviation from Curve .	−6	+8	+2	+1	+9	+5	+3	+8

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_s}{T_s}$.

Number:	1477.	1478.	1479.	1480.	1481.	1482.	1483.	1484.	1485.
Description:	50% 1452 plus 50% 1418.	25% 1452 plus 75% 1418.	25% 1453 plus 75% 1418.	50% 1453 plus 50% 1418.	75% 1453 plus 25% 1418.	75% 1452 plus 25% 1454.	50% 1452 plus 50% 1454.	25% 1452 plus 75% 1454.	75% 1453 plus 25% 1454.
Gravity, A.P.I. °	40·6	34·1	34·1	40·6	47·5	45·3	34·9	26·7	44·8
Sp. Gr. 60/60° F.	0·822	0·855	0·855	0·822	0·791	0·800	0·850	0·894	0·803
Aniline Pt., ° F.	134	142	143	137	132	109	95	84	—
Distillation:									
I.B.P., ° F.	160	188	178	154	153	136	150	190	138
10%	247	284	266	228	213	228	245	295	210
20	270	353	347	254	232	248	271	353	233
30	290	482	480	281	246	262	294	412	250
40	325	528	528	320	265	276	324	466	265
50	403	554	554	413	278	291	375	494	280
60	526	575	574	522	305	309	453	524	304
70	564	600	598	566	360	336	509	564	347
80	598	630	628	598	534	422	562	606	452
90	650	680	676	652	614	558	654	680	566
95	707	724	724	704	676	658	724	746	662
End Point	711	724	726	710	678	680	724	746	690
Recovery, %	98·0	97·5	98·0	98·5	97·5	98·0	97·5	98·0	98·0
Vol.Av.B.Pt.	431	520	515	428	342	335	415	509	331
a	436	530	525	434	350	348	438	545	346
Slope	5·04	4·95	5·12	5·30	5·01	4·12	5·11	4·81	4·45
Mol.Av.B.Pt.	390	480	473	383	301	305	373	471	297
Mol. Wt.	158	193	189	154	125	125	145	181	122
A	67·1	64·3	62·6	67·5	61·5	59·6	64·7	68·2	60·5
T_c Obs., ° F.	783	861	872	782	693	688	787	870	696
P_c Obs., lb./in.², Abs.	528	440	441	544	567	547	556	501	572
T_c Deviation from Curve	+6	−8	+7	+7	+11	+8	+8	−13	+18

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_c}{T_c}.$$

Number:	1486.	1487.	1488.	1489.	1490.	1422.	1495.	1496.
Description:	50% 1453 plus 50% 1454.	25% 1453 plus 75% 1454.	75% 1421 plus 25% 1454.	50% 1421 plus 50% 1454.	25% 1421 plus 75% 1454.	¼ each 1421, 1420, 1419.	¼ each 1452, 1420, 1419.	¼ each 1453, 1420, 1419.
Gravity, A.P.I. °	35·2	26·8	43·9	34·6	26·4	43·8	43·9	44·1
Sp. Gr. 60/60° F.	0·849	0·894	0·807	0·852	0·896	0·807	0·807	0·806
Aniline Pt., ° F.	—	—	—	—	—	—	—	—
Distillation:								
I.B.P., ° F.	150	176	100	110	120	120	180	166
10%	227	269	166	188	250	217	276	259
20	255	330	200	255	358	306	313	302
30	284	402	241	315	417	358	348	343
40	322	456	282	374	463	400	383	384
50	378	494	322	410	494	427	419	423
60	456	528	368	468	526	456	452	453
70	510	560	412	510	562	483	484	485
80	561	604	472	566	612	523	527	526
90	644	676	590	656	685	588	587	587
95	720	739	—	—	—	642	640	640
End Point	720	742	680	720	740	662	665	666
Recovery, %	98·0	98·5	96·5	97·0	97·5	98·0	98·5	98·5
Vol.Av.B.Pt.	409	480	346	416	482	415	423	419
a	432	519	360	440	522	416	422	418
Slope	5·21	5·10	5·30	5·85	5·44	4·51	3·89	4·10
Mol.Av.B.Pt.	366	448	301	363	436	380	395	389
Mol. Wt.	142	171	123	141	164	154	162	159
A	65·9	65·7	69·8	71·9	66·5	60·9	58·1	58·5
T_c Obs., ° F.	784	869	689	781	868	754	755	755
P_c Obs., lb./in.², Abs.	577	510	650	632	538	480	436	447
T_c Deviation from Curve	+11	+10	−5	0	+6	−2	−7	−3

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_c}{T_c}.$$

Number:	1497.	1498.	1499.	1500.	1501.	1502.	1454.	1455.	1503.
Description:	¼ each 1452, 1420, 1418.	¼ each 1453, 1420, 1418.	¼ each 1421, 1420, 1418.	¼ each 1452, 1420, 1454.	¼ each 1453, 1420, 1454.	¼ each 1421, 1420, 1454.	No. 1 Cycle Stock.	No. 2 Cycle Stock.	75% 1452 plus 25% 1455.
Gravity, A.P.I. ° .	41·3	41·5	41·0	37·6	37·9	37·4	19·6	13·7	42·3
Sp. Gr. 60/60° F..	0·819	0·818	0·820	0·837	0·835	0·838	0·937	0·975	0·814
Aniline Pt., ° F. .	—	—	—	—	—	—	73	—	—
Distillation:									
I.B.P., ° F. .	178	160	126	180	162	124	352	460	140
10% . .	270	250	228	272	254	236	442	520	233
20 . .	309	295	316	307	295	318	467	536	253
30 . .	345	336	363	340	334	360	488	550	270
40 . .	380	376	402	372	372	400	508	567	282
50 . .	416	416	432	403	399	420	530	584	295
60 . .	452	452	458	429	435	442	556	602	315
70 . .	492	490	494	460	460	466	588	625	355
80 . .	544	548	554	497	499	510	630	660	536
90 . .	616	620	624	586	586	610	690	720	610
95 . .	683	682	684	666	678	696	750	760 (93)	696
End Point .	693	692	687	694	698	700	752	—	704
Recovery, % .	98·5	98·0	98·0	98·5	98·5	98·0	98·0	—	98·0
Vol.Av.B.Pt. .	428	422	428	412	407	418	548	600	353
a . . .	432	427	433	429	424	434	607	682	369
Slope . .	4·32	4·62	4·95	3·92	4·15	4·67	3·10	2·50	4·71
Mol.Av.B.Pt. .	395	386	388	384	376	381	528	585	316
Mol. Wt. . .	159	155	156	152	148	150	200	218	128
A . . .	58·5	59·1	63·4	58·3	58·6	63·7	57·0	55·7	63·1
T_c Obs., ° F. .	774	767	770	772	771	770	941	1002	715
P_c Obs., lb./in.², Abs. . .	454	467	500	472	488	522	399	373	579
T_c Deviation from Curve . .	+1	0	−4	+3	+7	−5	+4	+7	+11

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_c}{T_c}.$$

Number :	1504.	1505.	1506.	1507.	1508.	1509.	1510.	1511.
Description :	50% 1452 plus 50% 1455.	25% 1452 plus 75% 1455.	75% 1453 plus 25% 1455.	50% 1453 plus 50% 1455.	25% 1453 plus 75% 1455.	75% 1421 plus 25% 1455.	50% 1421 plus 50% 1455.	25% 1421 plus 75% 1455.
Gravity, A.P.I. °	31·3	21·9	42·5	31·5	22·0	41·5	30·9	21·7
Sp. Gr. 60/60° F.	0·869	0·922	0·813	0·868	0·922	0·818	0·871	0·924
Aniline Pt., ° F.	—	—	—	—	—	—	—	—
Distillation :								
I.B.P., ° F. .	160	194	140	156	170	106	114	120
10% . .	248	282	213	227	264	168	185	262
20 . .	272	350	235	252	340	208	254	400
30 . .	296	474	251	276	482	248	320	490
40 . .	330	536	266	311	530	290	390	530
50 . .	424	556	282	406	554	332	460	556
60 . .	536	576	304	530	576	382	526	578
70 . .	568	602	350	565	600	444	568	606
80 . .	602	636	530	598	634	538	610	640
90 . .	662	696	606	664	696	634	682	706
95 . .	732	756	684	732	750	—	—	—
End Point .	738	756	702	736	750	710	736	750
Recovery, % .	98·5	98·0	98·0	98·5	98·5	97·0	97·0	98·5
Vol.Av.B.Pt. .	440	522	340	428	519	365	443	524
a . . .	469	575	358	458	571	380	473	576
Slope . .	5·19	5·19	4·91	5·47	5·40	5·83	6·21	5·55
Mol.Av.B.Pt. .	397	479	301	381	473	313	385	476
Mol. Wt. . .	151	179	123	146	177	126	146	177
A . . .	69·0	64·5	63·4	69·6	66·1	73·1	75·8	70·5
T_o Obs., ° F. .	817	916	708	816	913	711	814	894
P_o Obs., lb./in.², Abs. . .	583	496	601	607	513	679	661	539
T_o Deviation from Curve .	+6	+6	+16	+17	+7	−5	−1	−16

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_o}{T_o}.$$

Number :	1512.	1513.	1514.	1515.	1516.	1517.	1518.	1519.	1520.
Description :	75% 1420 plus 25% 1455.	50% 1420 plus 50% 1455.	25% 1420 plus 75% 1455.	75% 1419 plus 25% 1455.	50% 1419 plus 50% 1455.	25% 1419 plus 75% 1455.	75% 1418 plus 25% 1455.	50% 1418 plus 50% 1455.	25% 1418 plus 75% 1455.
Gravity, A.P.I. °.	34·7	27·0	20·0	29·3	23·8	18·6	24·3	20·7	17·1
Sp. Gr. 60/60° F..	0·851	0·892	0·934	0·880	0·911	0·942	0·908	0·930	0·952
Aniline Pt., ° F. .	—	—	—	—	—	—	—	—	—
Distillation :									
I.B.P., ° F. .	360	364	376	456	450	454	481	458	468
10% . .	392	404	434	505	506	510	519	515	518
20 . .	404	422	466	518	522	528	534	532	536
30 . .	414	440	493	530	524	541	548	548	549
40 . .	424	460	522	545	550	556	562	562	565
50 . .	436	483	549	560	564	572	578	578	580
60 . .	452	518	575	576	582	590	596	586	598
70 . .	474	560	600	593	605	614	618	624	620
80 . .	510	604	640	622	634	648	649	658	654
90 . .	604	670	696	666	688	702	705	689	710
95 . .	676	736	757	718	730	—	—	—	758
End Point .	698	736	757	726	730	754	740	747	758
Recovery, % .	98·5	98·5	98·5	98·5	96·0	98·0	98·0	97·5	98·0
Vol.Av.B.Pt. .	464	511	554	571	577	588	594	591	595
a . . .	481	546	611	591	617	648	630	642	662
Slope . .	2·65	3·32	3·28	2·01	2·28	2·40	2·32	2·18	2·40
Mol.Av.B.Pt. .	448	489	532	559	563	574	580	578	581
Mol. Wt. . .	179	190	202	230	224	222	234	227	223
A . . .	50·3	53·6	54·6	48·5	49·5	53·0	51·0	50·9	52·1
T_c Obs., ° F. .	821	883	942	915	944	972	951	972	977
P_c Obs., lb./in.², Abs. . .	360	379	379	290	310	342	307	321	335
T_c Deviation from Curve . .	−1	−1	+2	−8	−1	+2	−4	+7	−3

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_c}{T_c}.$$

Number:	1521.	1522.	1523.	1524.	(This data from International Critical Tables.)		
Description:	50% 1454 plus 50% 1455.	50% 1419 plus 50% 1454.	½ each 1452, 1420, 1455.	½ each 1453, 1420, 1455.	Hexane. C_6H_{14}.	Heptane. C_7H_{16}.	Octane. C_8H_{18}.
Gravity, A.P.I. °	16·5	26·9	35·3	35·3	—	—	—
Sp. Gr. 60/60° F.	0·956	0·893	0·848	0·848	0·660	0·684	0·707
Aniline Pt., ° F.	—	—	—	—	—	—	—
Distillation:							
I.B.P., ° F.	390	386	170	168	—	—	—
10%	476	468	275	250	—	—	—
20	500	490	310	298	—	—	—
30	522	507	348	338	—	—	—
40	540	526	382	378	—	—	—
50	560	543	415	416	—	—	—
60	584	563	454	456	—	—	—
70	614	587	500	496	—	—	—
80	651	620	552	550	—	—	—
90	718	673	632	628	—	—	—
95	—	730	698	694	—	—	—
End Point	759	730	722	714	—	—	—
Recovery, %	98·0	97·5	98·5	98·5	—	—	—
Vol.Av.B.Pt.	578	556	434	426	156	209	256
a	649	586	453	446	169	211	252
Slope	3·02	2·56	4·46	4·73	—	—	—
Mol.Av.B.Pt.	559	540	400	389	—	—	—
Mol. Wt.	211	216	157	152	—	—	—
A	56·5	51·7	61·7	61·0	—	—	—
T_c Obs., ° F.	973	924	791	793	455	512	565
P_c Obs., lb./in.², Abs.	384	331	491	503	—	—	—
T_c Deviation from Curve	+3	+5	−3	+6	+1	+2	+1

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$$A = \frac{M P_c}{T_c}.$$

Data Source :	International Critical Tables.			McKee and Parker.[2]				
Description :	Di-*iso*-Butyl, C_8H_{18}.	Benzene, C_6H_6.	Toluene, C_7H_8.	Norm. Octylene, C_8H_{16}.	Diallyl, C_6H_{10}.	*o*-Xylene, C_8H_{10}.	*m*-Xylene, C_8H_{10}.	*p*-Xylene, C_8H_{10}.
Sp. Gr. 60/60° F.	0·693	0·878	0·866	0·722	0·688	0·879	0·865	0·861
Vol.Av.B.Pt. .	229	175	231	253	139	291	282	280
a	228	242	287	255	165	344	331	327
T_c Obs., ° F. .	531	551	609	581	454	677	654	652
T_c Deviation from Curve .	−2	0	+1	+13	+6	+1	−6	−4

a = (Specific Gravity) (Volumetric Average Boiling Point + 100).

$A = \frac{M P_c}{T_c}$.

APPENDIX II.

TYPICAL DATA SHEETS SHOWING THE DIFFERENCE BETWEEN THE MAXIMUM TEMPERATURE, MAXIMUM PRESSURE, AND CRITICAL POINT AS WELL AS THE SPREAD OF THE CRITICAL REGION IN TEMPERATURE AS INDICATED BY THE RED COLOUR CHANGE. ALSO, THE EFFECT OF VARYING THE FLOW RATE ON THE OBSERVED CRITICAL PRESSURE OF A FRACTION HAVING A HIGH CRITICAL TEMPERATURE IS SHOWN.

Stock No. 1424.
50% Mid-Continent Gas Oil plus 50% Cracked Naphtha.

Pressure (Gauge).	Temperature.		Remarks.
	Bottom T.C.	Top T.C.	
562	766	754	Critical red
555	768	758	" "
549	771	763	Critical red plus
554	766	759	*Critical* red
558	762	757	Critical red
562	758	753	Critical red minus
557	765	756	*Critical* red
549	770	762	Critical red plus
552	766	761	*Critical* red
555	761	757	*Critical* red
420	802	793	Maximum temperature. Bottom of observation chamber

T_c = 761° F.
P_c = 565 lb. per square inch, absolute.
T_m = about 802° F.
P at T_m = about 430 lb. per square inch, absolute.
P_m = about 572 lb. per square inch, absolute.
T at P_m = about 756° F.

The maximum temperature was taken as the point at which the last trace of liquid could be seen near the bottom of the observation chamber.

Stock No. 1455.
No. 2 Cycle Gas Oil.

Pressure (Gauge).	Temperature.		C.c. per sec.	Remarks.
	Bottom T.C.	Top T.C.		
230	891	877	8·4	Point on boiling line
253	913	897	8·1	,, ,, ,,
302	932	927	7·5	,, ,, ,,
345	965	951	7·7	,, ,, ,,
373	984	969	7·7	,, ,, ,,
387	1007	996	7·0	Red plus
390	1001	991	6·6	Red critical
386	998	986	6·8	Below critical
388	1004	990	8·6	Red critical
383	1008	995	8·5	*Red* critical
378	1011	998	8·1	Above critical
373	1007	997	9·4	Red critical
378	1003	991	10·5	Below critical
378	1006	994	10·9	*Red* critical
375	1009	996	10·4	,, ,,
367	1010	1000	10·0	Above critical
362	1011	1000	12·6	,, ,,
368	1006	997	11·6	*Red* critical
368	998	991	11·6	Just below critical
368	1003	991	13·0	,, ,, ,,
369	1004	993	13·0	Red minus
368	1007	995	12·8	*Red* critical
369	1008	996	12·0	,, ,,
365	1009	998	11·6	Above critical
363	1007	996	13·0	*Red* critical
365	1007	996	13·9	,, ,,
364	1008	996	13·6	Red critical
361	1003	991	16·0	Below critical
361	1001	989	15·4	,, ,,

$T_c = 1002°$ F.
$P_c \leq 373$ lb. per square inch, absolute.

This run shows clearly that as the flow rate increased the critical pressure decreased, making the true critical pressure somewhat uncertain. This gas oil did not crack readily and so could be measured with considerable accuracy. Other virgin gas oils having critical temperatures in the same region and predicted critical pressures of less than 250 lb. per square inch, absolute, showed observed critical pressures of over 500 lb. per square inch, absolute, indicating that appreciable cracking was occurring.

APPENDIX III.

CRITICAL TEMPERATURE OF A HEAVY FRACTION BY EXTRAPOLATION.

The estimation of the critical temperature of a solvent-refined SAE-20 oil by extrapolation of measurements made on kerosine blends is carried out as follows :

Let y be the measured critical temperature and x the corresponding volume per cent. We assume $y = a + bx + cx^2$, and determine a, b, and c by the method of least squares. We form the following table :

x.	$x^2 10^{-2}$.	$x^3 10^{-4}$.	$x^4 10^{-6}$.	y.	$xy 10^{-4}$.	$x^2y 10^{-6}$.
0	0	0	0	758	0	0
20	4·00	0·8	1·6	844	1·688	3·376
30	9·00	2·7	8·1	882	2·646	7·938
40	16·00	6·4	25·6	916	3·664	14·656
50	25·00	12·5	62·5	945	4·725	23·625
Σ 140	$5·4 \times 10^3$	$2·24 \times 10^5$	$9·78 \times 10^6$	4345	$1·2723 \times 10^5$	$4·9595 \times 10^6$

From the theory of least squares we then have the following simultaneous linear equations for a, b, and c :

$$5a + 140b + 5·4 \times 10^3 c = 4·345 \times 10^3.$$
$$140a + 5·4 \times 10^3 b + 2·24 \times 10^5 c = 1·2723 \times 10^5.$$
$$5·4 \times 10^3 a + 2·24 \times 10^5 b + 9·78 \times 10^6 c = 4·9595 \times 10^6$$

Eliminating a from the first and third equations, we find :

$$7·4b + 364c = 27·85.$$
$$3·64b + 197·4c = 13·345.$$

Eliminating b, we find for c :

$$c = -1·930 \times 10^{-2}.$$

We then calculate b, and finally a, and obtain :

$$b = 4·71289.$$
$$a = 757·88.$$

Thus, $y = 757·88 + 4·71289x - 0·0193x^2$.
We then calculate y and find :

x.	y (calc.).	y (obs.).	v.
0	757·88	758	0·12
20	844·42	844	−0·42
30	881·90	882	0·10
40	915·52	916	0·48
50	945·27	945	−0·27
100	1036·2	?	—

To calculate the probable error of the extrapolated value 1036·2, we use the following formulæ :

$$r_e = 0{\cdot}6745\sqrt{\frac{\Sigma v^2}{n-3}},\ n = 5$$

$$r(\epsilon) = r_e\sqrt{\frac{A_{11}(\epsilon)}{D}}$$

in which $r(\epsilon)$ = probable error at any point $x = \epsilon$.

$$D = \begin{vmatrix} n & \Sigma x & \Sigma x^2 \\ \Sigma x & \Sigma x^2 & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^3 & \Sigma x^4 \end{vmatrix}$$

$$A_{11}(\epsilon) = \begin{vmatrix} \Sigma(x-\epsilon)^2 & \Sigma(x-\epsilon)^3 \\ \Sigma(x-\epsilon)^3 & \Sigma(x-\epsilon)^4 \end{vmatrix}$$

We find $D = 2{\cdot}716 \times 10^9$

$$A_{11}(100) = 2{\cdot}241 \times 10^{11}$$
$$\Sigma v^2 = 0{\cdot}5041$$
$$r_e = 0{\cdot}3386$$
$$r(100) = 3{\cdot}1$$

Therefore, we find the extrapolated critical temperature of the SAE-20 oil to be 1036 $\pm$ 3° F., on the basis of volume per cent.

Taking 0·8095 and 0·8838 as the measured densities of the kerosine and the SAE-20 oil, we calculate :

Volume, per cent.	Weight, per cent.
0	0
20	21·44
30	31·88
40	42·13
50	52·19

Following the same procedure as before, we obtain :

x.	y (calc.).	y (obs.).	v.
0	757·86	758	0·14
21·44	844·54	844	−0·54
31·88	881·85	882	0·15
42·13	915·40	916	0·60
52·19	945·36	945	−0·36
100	1047·1	?	—

Calculating the probable error as before, we find :

$$D = 3{\cdot}499 \times 10^9$$
$$A_{11} = 2{\cdot}293 \times 10^{11}$$
$$\Sigma v^2 = 0{\cdot}8233$$
$$r_e = 0{\cdot}4328$$
$$r(100) = 3{\cdot}5$$

The extrapolated critical temperature of the SAE-20 oil, on the basis of weight per cent., is therefore 1047 $\pm$ 3·5° F.

THE THERMAL AND TIME FACTORS IN CARBURATION.*

By James Small, D.Sc., Ph.D.

The word carburettor literally means an apparatus for charging some medium with carbon. In practice the medium is the air entering the induction system of an internal-combustion engine and the carbon is that of the fuel. The name "carburettor" has come to apply to that apparatus the function of which is to measure out the petrol supplied to an engine and to regulate the proportion of its mass to that of the air supply. The process of carburation has been thought of, therefore, only as one of hydrodynamics, bearing on the flow and confluence of two streams of different fluids. But the process of charging the air with petrol is also a matter involving the thermal condition of the fluids and of the mixture, and therefore carburation might well be regarded as the function of the whole induction system. Hence we may justifiably speak of the thermal and time factors in carburation.

The total energies of the fluids before mixing are equal to the total energy of the mixture formed. The kinetic energies, however, are from this point of view either negligible in themselves or suffer a negligible change during mixing. Hence, from simple thermodynamic considerations, we may show that the sum of the total heats of the fluids before mixing is equal to the total heat of the mixture formed.

According to Dalton's law, the vaporized petrol occupies the whole volume of the mixture, but contributes only its partial pressure to the total pressure of the mixture, provided the fluids are in thermal equilibrium.

It is to be feared that even when the charge enters the cylinder the constituents are further from this condition than is generally supposed. Leaving over the discussion of that point, let us consider in the meantime fuel–air mixtures which are in a condition of equilibrium. It is a matter of great interest to study the thermal properties of such mixtures.

The total heat of dry water vapour at low pressures is very nearly a linear function of temperature only. This fact enabled R. Mollier (*Z.V.D.I.*, July 20, 1929), to construct a most useful chart of total heat and vapour content for humid atmospheric air (now referred to on the Continent as the Mollier $i-x$ Diagram).

For many hydrocarbons, while their thermal properties are not so well established as those of water, it is found that, to a sufficient degree of approximation, the linear law of total heat of vapour applies. Even petrol is approximately subject to this law at atmospheric and sub-atmospheric pressures. Hence it is possible to construct diagrams of the Mollier form for the mixtures of such fluids with pure air.

* Paper received July 3rd, 1936.

Let the total heat in C.H.U. of 1 lb. of the dry or super-heated vapour of a fuel be expressible by :—

$$H_f = a + b\,.\,t$$

where $t°$ C. is the temperature and a and b are constants.

If P is the total pressure of a mixture of 1 lb. of air and x lb. of fuel the vapour pressure of which is p_f, then,

$$x = \frac{M_f}{M_a} \cdot \frac{p_f}{P - p_f}$$

where M_f and M_a are the molecular weights of the fuel-vapour and air respectively.

If p_f' is the saturation pressure corresponding to the existing temperature t, then x', the weight of fuel which saturates 1 lb. of air at the total pressure P and temperature t, is :—

$$x' = \frac{M_f}{M_a} \cdot \frac{p_f'}{P - p_f'}$$

If the quantity of fuel present per lb. of air is greater than this, then the excess is present in liquid form. If the total pressure P is changed, the value of x' is changed. Any mixture of 1 lb. of air and x ($< x'$) lb. of fuel has total heat $0{\cdot}24t + x(a + bt)$, where 0·24 is the specific heat of air.

These facts permit of the construction of a chart of the Mollier form. Such a chart for mixtures of ethyl alcohol and air is found in Fig. 1.

Saturation curves are drawn for different total pressures. The lines of constant fuel content are vertical and equally spaced, and the lines of constant temperature diverge towards the right in the dry region at such a rate as to keep the lines of constant total heat parallel and equally spaced. At any given total pressure the region lying below and to the right of the corresponding saturation curve represents a condition of wetness in the mixture, and the constant temperature lines in this region may, for practical purposes, be regarded as running parallel to the total heat lines.

Such devices as the "strangler valve" operate to cause an excessive flow of fuel into the air-stream, but if at the same time they cause a fall in pressure at the carburettor, they are helping to promote a condition conducive to better vaporization. For suppose that, due to partial preheating, 19·6 C.H.U. of heat are available per lb. of air. At a total pressure of 760 mm. this would enable 0·071 lb. of ethyl alcohol (Fig. 1) to be evaporated, and the temperature of the resulting mixture would be 15° C.—for practical purposes the temperature of the atmosphere. But if the pressure is reduced to half an atmosphere (380 mm.), the same total heat, if given time, not only enables a greater proportion of the fuel to be evaporated—namely, 0·082 lb. per lb. of air—but also results in the low temperature of 6° C. Heat must flow from the atmosphere through to the region of such low temperature, and this heat increases the relative amount of fuel vaporized. If such flow of heat could continue until the temperature approximated to 15° C. all the fuel in the chemically correct mixture would be vaporized.

These facts, applying to conditions of thermal equilibrium, indicate the influences which make for vaporization, and they are effective also in the case of petrol, which differs from a substance like ethyl alcohol in having

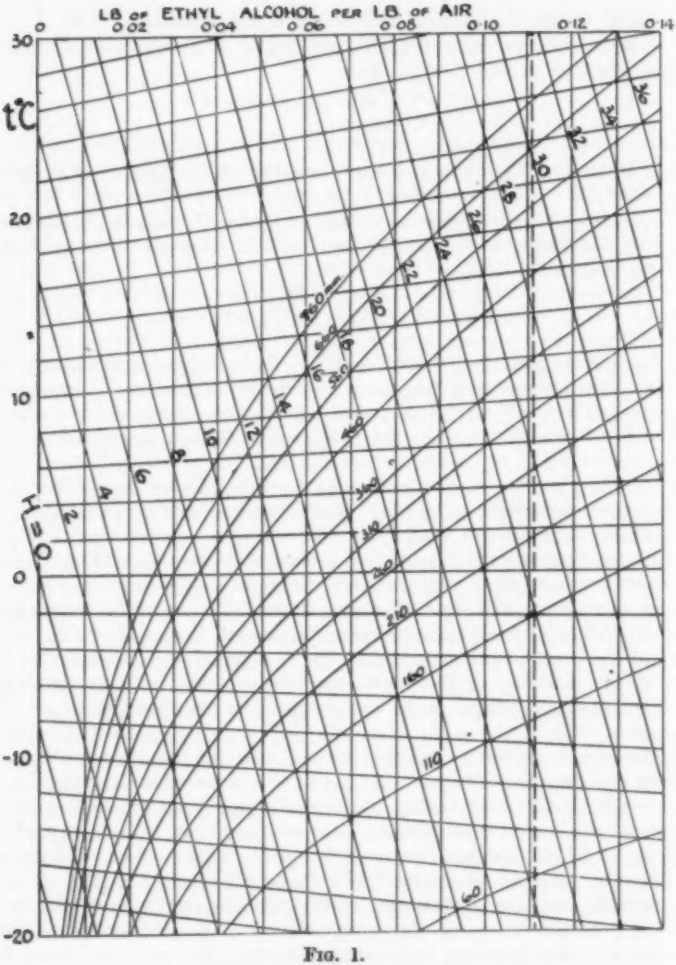


FIG. 1.

CARBURATION CHART FOR ETHYL ALCOHOL.

no fixed boiling point and in having a latent heat which is not simply defined.

Our problem with petrol may be tackled in the following way. Suppose a little liquid petrol containing no dissolved air to be enclosed in a cylinder with close-fitting piston under a given pressure. Let the petrol be

vaporized completely by heating while the piston is adjusted to keep the pressure constant. That temperature at which vaporization is just completed is the equilibrium temperature corresponding to the given pressure. Now, if the equilibrium temperature of a petrol is known over a range of pressures, the dew point (*i.e.* the temperature at which liquid petrol would begin to form) of a given mixture of air and this petrol is fixed. Conversely, it is possible to find the temperature necessary in a mixture formed by passing liquid petrol in limited quantity into an air stream (as in carburation), in order to secure the evaporation of the whole of that quantity.

The total heat of completely vaporized petrol is approximately expressible as a linear function of temperature. Hence it becomes possible to apply the *total heat — vapour content* or $H - x$ chart to the purpose of fixing the minimum total heat and temperature for supporting the complete volatilization of the petrol in the mixture leaving the carburettor.

Equilibrium temperatures ($T°$ absolute) and pressures (p_f') are closely expressible by equations of the form :—

$$\log p_f' = A - \frac{B}{T}$$

If the equation of total heat of vaporized petrol and its virtual molecular weight are known, it is possible to construct the chart.

Fig. 2 is constructed for a petrol which has the following properties :—

$$\log p_f' = 7{\cdot}425 - \frac{1953{\cdot}7}{T} \quad (p_f' \text{ in mm. of mercury and } T. \text{ in } ° \text{ C. abs.})$$

$$H = 75 + 0{\cdot}41t \text{ C.H.U/lb.}$$

and a molecular weight of 114.*

The total heat of a mixture of 1 lb. of air and x lb. of this petrol, completely vaporized, is given by :—

$$H_m = 0{\cdot}24t + x(75 + 0{\cdot}41t)$$

It is worthy of note that the heat for vaporizing at 760 mm. total pressure, the chemically correct proportion of this petrol (indicated by the vertical dotted line on Fig. 2), if supplied by preheating the air, demands a minimum air-temperature of 59° C., and any temperature less than 37° C. in the induction manifold could not support a completely vaporized mixture. The time-factor in establishing thermal equilibrium is so great that it must be emphasized that in practice temperatures very much greater than these would be involved if complete vaporization were the aim in view—as it might be if perfect distribution to the cylinders of a multi-cylinder engine were the sole consideration. It is doubtful whether complete vaporization in the induction system can ever be achieved in practice.

If a high degree of vaporization is looked upon as a means to easy ignition, then it is the condition towards the end of compression that

* These figures are submitted for the sake of illustrating the construction of the chart; but they have been chosen as comparable with those of a good grade petrol in common use, after reference to various sources.

matters. If a mixture of air and fuel in chemically correct proportions and in a condition of thermal equilibrium is adiabatically compressed, it may be shown by the construction of $H - \phi$ charts that the work of compression carries the mixture into the dry and superheated region. And, on the face of it, it might seem reasonable to conclude that in the engine under running conditions, evaporation cannot but be complete

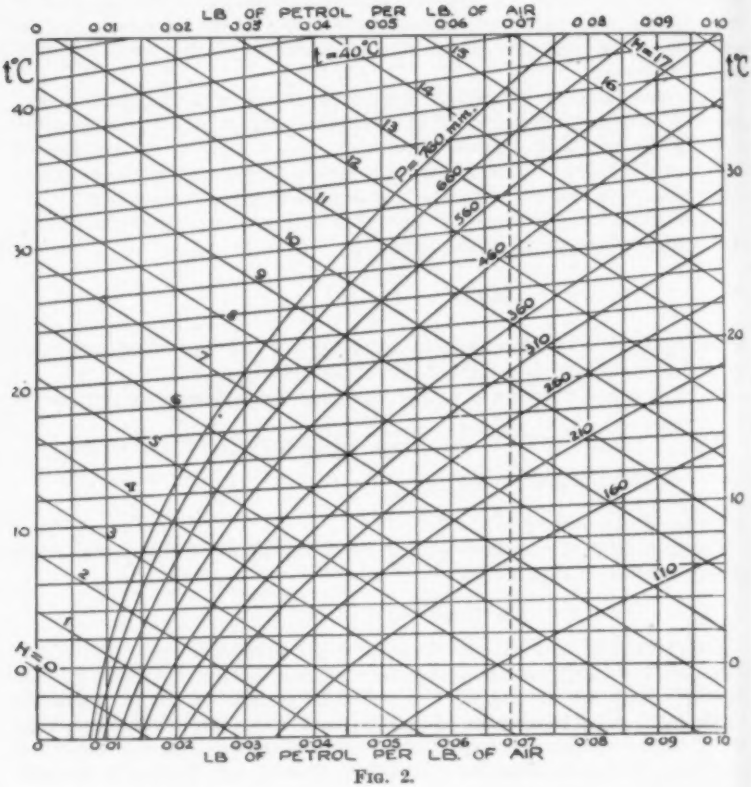


FIG. 2.

at the point of ignition. But in fact such a conclusion is not supported by the evidence.

RATES OF EVAPORATION IN AIR.

To what extent is evaporation actually carried in the induction system? To find at least an approximate answer to this question the writer erected in a vertical position an air channel, 2 in. square in section. Two opposite sides were of glass for observing the nature of the liquid stream, which was supplied from a jet placed centrally in the channel (see Fig. 11). Air could be drawn upwards through the channel at steady velocities up to 40 ft./sec. At a point 27 in. above the jet a sampling pipe was inserted

across the stream. This took the form shown in Fig. 3. The small tube 1 had holes along the top generating line, away from the rising stream of petrol, and on the under-side it was shielded by the outer piece 2, formed from a short length of larger tubing. In this way a sample of air and the vaporized petrol associated with it could be slowly drawn into a gas holder without any liquid particles being introduced.

At different air speeds, and with the air–petrol ratio at about 15 to 1, samples were taken. Since the inside of the channel at the sampling pipe was at a lower temperature than the air outside, no separation of petrol due to condensation in the connections was possible.

With the air entering the channel at room temperature, if the petrol used were that to which Fig. 2 refers, 2 per cent. of an equilibrium mixture should be petrol. In actual fact the proportion of hydrocarbons in the sample was so small as not to be amenable to the finer methods of gas analysis. And even when the sample was expelled into a bunsen flame, the presence of hydrocarbons could not be detected.

It may be stated that some of the petrol was carried as liquid particles beyond the sampling point, and some struck the sides of the channel below

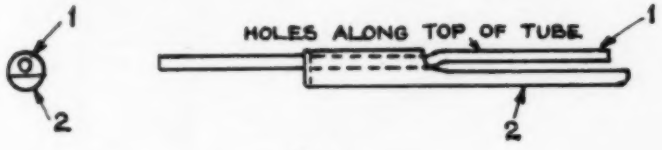


FIG. 3.

the sampling point and was caused to flow upwards in the form of a liquid film. In other words, the conditions were similar to what we should have in practice if a long, vertical induction pipe were fitted. In the experiment the conditions were more conducive to a higher degree of vaporization than in an engine with the same induction air temperature.

The air entering the channel was next heated to 50° C. and samples were taken. Still the samples would not respond to the combustion process in the Bone and Wheeler apparatus, and there was comparatively little trace of hydrocarbons in the air. Under the conditions of air temperature, etc., holding in this case, on the assumption of thermal equilibrium, Fig. 2 might lead us to expect that some 6 per cent. of the gaseous mixture should be petrol.

Such evidence of the relative slowness of the evaporation process causes us to seek a positive means of measuring the rates of evaporation from the surface of a volatile liquid, such as petrol, into a current of air.

MEANS OF MEASURING RATES OF EVAPORATION IN AN AIR-STREAM.

It is obvious that there are many practical difficulties to be overcome: obtaining a surface which remains stable as the air blows over it, controlling surface temperature, measuring the volume or weight of the petrol evaporated under continuous running conditions, eliminating the aerodynamic effects set up by the containing vessel, and so on.

After many methods were tested, it was decided to stretch a silk gauze over a frame in the containing vessel, and to measure the rates of evaporation from its wetted surface. Tests were made to find whether the readings thus obtained were likely to be noticeably different from the rates of evaporation from a free liquid surface. Although readings from the free liquid surface were liable to be influenced by ripples, spilling over the rear edge of the vessel, and so on, and the surface temperatures were difficult to read, careful measurements tended to show that the rate of evaporation may be less from the gauze than from the free surface, but not by an appreciable amount. Only from the gauze was it possible to obtain satisfactorily consistent results.

The vessel containing the volatile liquid was rectangular, 12 in. long, 2 in. broad and $\frac{5}{8}$ in. deep. The gauze was stretched on a brass frame made to fit the inside of the pan, and placed at a level about 0·02 in. below the top edge. It was the type of gauze used sometimes in oil-engine filters—woven from a wood product with a fibre of about 0·0025 in.

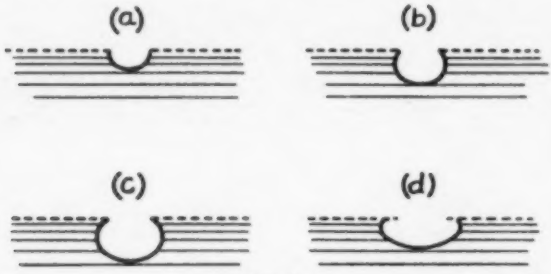


FIG. 4.

diameter, and having 50 meshes to the inch. The fibre was completely wetted by the liquid in the pan. A hole of about $\frac{3}{16}$-in diameter was cut in the gauze. This formed an indicator of the volume of liquid evaporated. The principle of its operation is as follows.

As evaporation takes place from the surface of the wetted gauze, the liquid level at the hole falls, while the liquid elsewhere clings to the gauze. At (*a*) Fig. 4 this effect is commencing and, as the liquid is withdrawn from the surface by evaporation, the recess becomes larger as at (*b*) and (*c*); but when a certain formation as at (*c*) is reached, the surface tension is no longer able to hold the body of the liquid to the edge of the gauze at the hole, and suddenly there is a jump to the formation (*d*). This can easily be observed through a window in the side of the channel, and so this stage in the evaporation can be accurately timed. When liquid is added to the pan the bubble fills up and in due course the "jump" again takes place. In the interval the quantity of liquid evaporated is the quantity added.

The containing pan 1 (Fig. 5) was set into an aperture cut in the bottom of a wind-channel of about 2 ft. square section, ordinarily used for aerodynamic experiments. Quantities of the liquid under test were contained in the burette 2 and in the stoppered bottle 3. The bottle 4 was used

when necessary in draining the pan. A copper–constantan thermocouple had one junction 5 inserted into the air stream, and the other junction 6 carried on an adjustable rod 7 and kept in contact with the gauze. This junction was made in the form of a stirrup with the wires on the cross-piece flattened horizontally, to minimize the aerodynamic disturbance

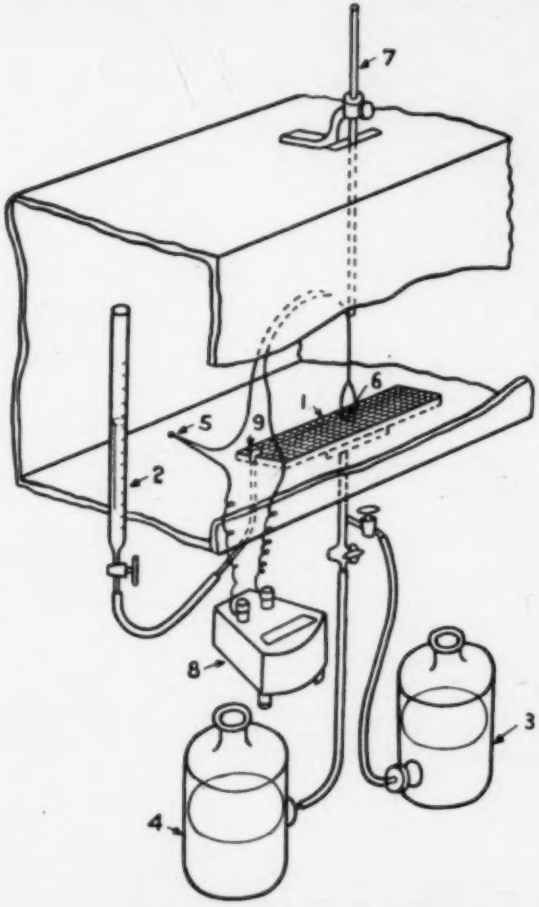


FIG. 5.

which it might tend to set up at the surface. The reading on the millivoltmeter 8 gave the difference in temperature between the air and the liquid. The actual temperature of the air was noted on a thermometer.

It was found that the reading of junction 6 when placed midway along the pan was, for practical purposes, the average over the whole surface.

A small brass tube 9 passing through the bottom of the channel and bent

over the pan was connected to the burette. By this means measured volumes of liquid were passed on to the gauze from the burette during the tests. In expressing rates of evaporation of pure liquids in air, it is most useful to give values of $\frac{W}{p}$, where W is the mass of liquid evaporated in unit time from unit surface, and p is the fall in vapour pressure from the surface to the air-stream. Petrol, however, being a complex mixture

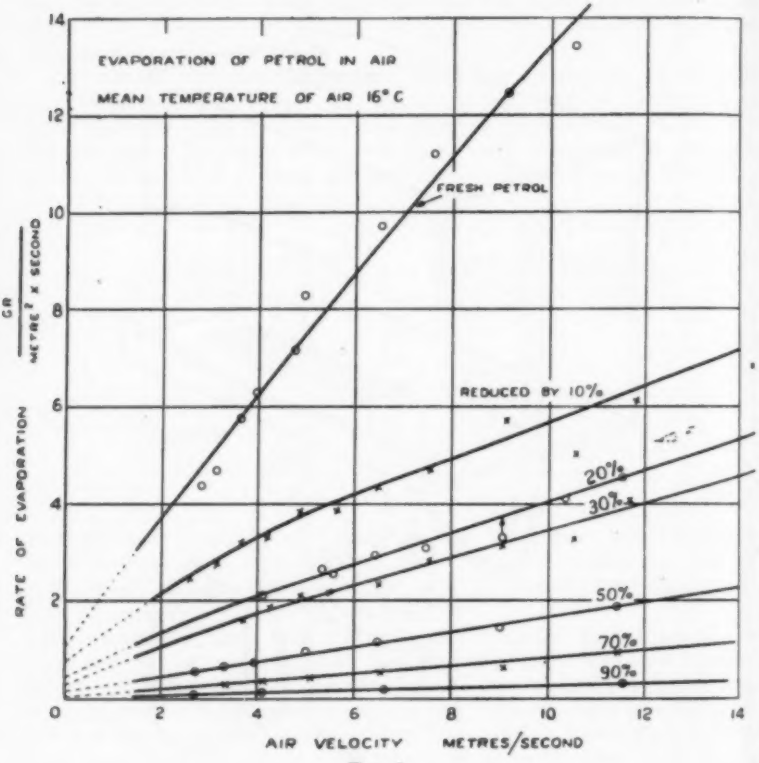


FIG. 6.

of mutually soluble components, its total vapour pressure changes as the lighter fractions are removed by vaporization. The following was therefore the method adopted in the course of these observations. A certain petrol was taken and samples were prepared by evaporation. Thus a quantity of the freshly drawn liquid was reduced by evaporation to 90 per cent. of its weight, another to 80 per cent. of its weight, and so on.

Each sample was subjected to evaporation tests at different air-speeds, and the figures of Table I and the curves of Fig. 6 are the result.

In Table II are the observations of evaporation in still air, and the

TABLE I.

Evaporation of Petrol in an Air Current. (*Area of wetted surface = 155 cm.*)

Condition of petrol.	Air velocity.		Thermo-couple milli-volt-meter readings Divisions.	Air temp. (° C.).	Temp. of liquid surface (° C.)	Barometer reading.		Temp. at burette (° C.)	Density of liquid (corrected) (gm./cm.³)	Volume evaporated. (cm.³).	Time of evaporation.		Rates of evaporation.		
	ft./sec.	$\frac{\text{m.}}{\text{sec.}}$ (V.)				ins.	mm.				min.	sec.	$\frac{\text{c.c.}}{\text{sec.}}$.	$\frac{\text{c.c.}}{\text{m.}^2 \times \text{sec.}}$.	$\frac{\text{gm.}}{\text{m.}^2 \times \text{sec.}}$.
As taken from the pump	34·5	10·51	20·0	16·6	2·0	29·38	746	18·0	0·730	10·0	0	35·2	0·284	18·30	13·4
	29·9	9·12	19·5	16·4	2·2	,,	,,	18·0	,,	10·0	0	39·4	0·254	16·40	12·4
	24·9	7·60	19·7	16·4	2·0	,,	,,	18·0	,,	10·0	0	42·0	0·238	15·35	11·2
	21·3	6·50	18·6	16·3	2·7	,,	,,	17·8	,,	10·0	0	48·4	0·206	13·30	9·69
	16·1	4·91	17·3	16·3	3·7	,,	,,	17·8	,,	10·0	0	57·0	0·175	11·30	8·24
	15·5	4·73	17·0	16·25	3·8	,,	,,	17·8	,,	10·0	1	6·0	0·152	9·80	5·15
	13·0	3·96	15·8	16·05	4·5	,,	,,	17·6	,,	10·1	1	16·0	0·133	8·58	6·26
	12·0	3·66	15·6	16·0	4·6	,,	,,	17·6	,,	10·0	1	21·8	0·122	7·86	5·74
	10·2	3·11	15·1	16·0	5·0	,,	,,	17·6	,,	10·0	1	41·2	0·099	6·39	4·66
	9·2	2·81	15·6	15·85	4·5	,,	,,	17·6	,,	10·0	1	48·0	0·0925	5·96	4·35
Previously reduced 10% in weight by evaporation	47·1	14·35	13·7	14·8	4·8	29·38	746	19·0	0·738	10·0	1	7·5	0·143	9·22	6·81
	38·7	11·80	14·0	14·8	4·6	,,	,,	19·0	,,	10·0	1	15·8	0·128	8·26	6·09
	34·6	10·55	13·7	14·5	4·5	,,	,,	19·0	,,	10·0	1	35·0	0·105	6·77	5·00
	29·9	9·11	11·0	14·5	6·5	,,	,,	19·0	,,	5·0	0	41·5	0·120	7·74	5·71
	24·7	7·53	12·0	14·5	5·7	,,	,,	18·8	,,	5·0	0	51·2	0·0977	6·30	4·65
	21·2	6·46	11·5	14·5	6·1	,,	,,	18·8	,,	5·01	0	55·0	0·912	5·89	4·34
	18·4	5·61	11·4	14·5	6·2	,,	,,	18·8	,,	5·0	1	1·6	0·0813	5·24	3·87
	15·9	4·85	11·4	14·5	6·2	,,	,,	18·8	,,	5·0	1	2·6	0·0799	5·15	3·80
	13·5	4·11	11·6	14·5	6·0	,,	,,	18·7	,,	5·0	1	12·2	0·0692	4·46	3·29
	11·9	3·63	11·7	14·6	6·1	,,	,,	18·7	,,	5·0	1	17·0	0·0650	4·19	3·09
	10·2	3·11	10·0	14·5	7·2	,,	,,	18·7	,,	5·0	1	28·0	0·0569	3·67	2·71
	8·5	2·59	9·0	14·5	7·9	,,	,,	18·7	,,	5·0	1	38·0	0·0510	3·29	2·43

TABLE I (*contd.*).

Evaporation of Petrol in an Air Current.

Condition of petrol.	Air velocity.		Thermo-couple milli-volt-meter readings Divisions.	Air temp. (° C.).	Temp. of liquid surface (° C.).	Barometer reading.		Temp. at burette (° C.).	Density of liquid (corrected) (gm./cm.³).	Volume evaporated (cm.³).	Time of evaporation.		Rates of evaporation.		
	ft./sec.	m./sec. (*V*).				ins.	mm.				min.	sec.	c.c./sec.	c.c./m.³ × sec.	gm./m.³ × sec.
Previously reduced 20% in weight by evaporation	37·8	11·51	11·8	15·3	6·7	29·75	756	17·4	0·747	5·0	0	53·0	0·0944	6·09	4·55
	34·0	10·36	12·2	15·5	6·6	,,	,,	17·8	,,	5·0	0	59·4	0·0842	5·44	4·06
	29·6	9·02	11·3	15·4	7·2	,,	,,	17·9	,,	5·58	1	21·6	0·0683	4·43	3·29
	24·5	7·47	10·0	15·6	8·3	,,	,,	18·2	,,	5·0	1	18·0	0·0639	4·18	3·08
	21·0	6·40	11·5	15·6	7·2	,,	,,	18·2	,,	5·0	1	22·0	0·0610	3·93	2·04
	18·2	5·55	9·6	15·6	8·6	,,	,,	18·5	,,	5·0	1	35·8	0·0522	3·37	2·52
	17·5	5·34	9·3	15·6	8·8	,,	,,	18·5	,,	5·0	1	32·0	0·0544	3·50	2·62
	13·4	4·09	8·4	15·6	9·5	,,	,,	18·7	,,	5·0	1	55·0	0·0435	2·81	2·10
Previously reduced 30% in weight by evaporation	38·3	11·68	11·0	18·0	9·9	30·06	763	20·5	0·756	5·0	1	0·2	0·0831	5·36	4·05
	34·5	10·51	11·0	18·0	9·9	,,	,,	20·5	,,	5·08	1	15·0	0·0678	4·37	3·30
	29·7	9·05	11·0	18·0	9·9	,,	,,	20·4	,,	5·03	1	17·5	0·0649	4·19	3·17
	24·8	7·56	9·8	17·9	10·8	,,	,,	20·7	,,	5·0	1	26·6	0·0578	3·72	2·81
	21·3	6·49	9·8	17·5	10·4	,,	,,	20·8	,,	5·02	1	45·0	0·0479	3·09	2·33
	17·9	5·46	8·3	17·4	11·3	,,	,,	20·7	,,	5·01	1	51·2	0·0451	2·91	2·20
	16·0	4·88	8·0	17·4	11·6	,,	,,	20·7	,,	5·08	1	58·0	0·0431	2·78	2·10
	13·8	4·21	7·9	17·4	11·6	,,	,,	20·7	,,	5·0	2	12·0	0·0379	2·44	1·84
	12·1	3·69	7·7	17·3	11·7	,,	,,	20·9	,,	5·0	2	31·2	0·0331	2·135	1·61

TABLE I (*contd.*).

Evaporation of Petrol in an Air Current.

Condition of petrol.	Air velocity.		Thermo-couple milli-volt-meter readings Divisions.	Air temp. (° C.).	Temp. of liquid surface (° C.).	Barometer reading		Temp. at burette (° C.).	Density of liquid (corrected) (gm./cm.³).	Volume evaporated. (cm.³).	Time of evaporation.		Rates of evaporation.		
	ft./sec.	m./sec. (V).				ins.	mm.				min.	sec.	c.c./sec.	c.c./m.² × sec.	gm./m.² × sec.
Previously reduced 50% in weight by evaporation	37·5	11·42	6·8	17·0	12·0	30·13	765	19·2	0·772	5·01	2	15·2	0·0371	2·39	1·85
	29·5	9·00	6·1	17·0	12·5	,,	,,	19·4	,,	5·01	2	56·0	0·02845	1·83	1·42
	21·2	6·46	6·0	16·75	12·35	,,	,,	19·5	,,	3·00	2	7·0	0·0236	1·52	1·18
	16·4	5·00	5·1	16·7	13·0	,,	,,	19·7	,,	3·04	2	42·2	0·0187	1·21	0·933
	13·0	3·96	4·2	16·7	13·6	,,	,,	20·0	,,	3·01	3	11·0	0·01575	1·02	0·786
	10·9	3·32	4·3	16·6	13·5	,,	,,	20·1	,,	3·01	3	44·2	0·0134	0·864	0·669
	8·9	2·71	3·9	16·6	13·7	,,	,,	20·5	,,	3·00	4	16·8	0·0117	0·755	0·584
Previously reduced by 70% in weight by evaporation	37·5	11·42	3·8	17·9	15·1	30·13	765	19·8	0·789	2·00	1	43·0	0·01942	1·251	0·989
	29·8	9·09	4·0	17·65	14·7	,,	,,	20·2	,,	2·01	2	27·0	0·01368	0·881	0·676
	21·4	6·53	3·3	17·5	15·1	,,	,,	20·4	,,	2·00	3	7·5	0·01067	0·688	0·543
	16·7	5·09	3·9	17·4	14·6	,,	,,	20·3	,,	2·00	4	9·0	0·00808	0·520	0·411
	13·4	4·09	2·9	17·3	15·2	,,	,,	20·4	,,	2·00	4	44·0	0·00704	0·454	0·358
	10·9	3·32	2·9	17·2	15·1	,,	,,	20·6	,,	2·00	5	43·0	0·00584	0·376	0·297
Previously reduced by 90% in weight by evaporation	37·9	11·54	2·7	16·15	14·2	30·15	766	18·6	0·808	1·20	3	24·0	0·00589	0·380	0·308
	21·7	6·61	2·3	15·85	14·2	,,	,,	18·6	,,	1·00	5	28·0	0·00305	0·197	0·159
	13·4	4·09	2·0	15·48	14·6	,,	,,	18·6	,,	0·50	4	34·4	0·00182	0·117	0·095
	8·9	2·71	1·8	15·30	14·0	,,	,,	19·2	,,	0·50	5	40·0	0·00147	0·095	0·0766

TABLE II.

Evaporation of Petrol in Still Air. (Area of horizontal wetted surface = 155 cm.²)

Condition of petrol.	Thermo-couple millivolt-meter readings. Divisions.	Air temp. (° C.).	Temp. of liquid surface (° C.).	Barometer reading.		Temp. at burette (° C.).	Density of liquid (corrected) (gm./cm.³).	Volume evaporated (cm.³).	Time of evaporation.		Rates of evaporation.		
				ins.	mm.				min.	sec.	$\frac{\text{c.c.}}{\text{sec.}}$	$\frac{\text{c.c.}}{\text{m.}^2 \times \text{sec.}}$	$\frac{\text{gm.}}{\text{m.}^2 \times \text{sec.}}$
As taken from pump	5·1	15·8	12·1	29·82	759	18·7	0·729	1·00	0	48	0·0208	1·342	0·979
	5·1	15·8	12·1	,,	,,	18·7	,,	1·00	0	53	0·0189	1·219	0·889
	6·8	16·0	11·0	,,	,,	19·0	,,	0·94	0	44	0·0214	1·380	1·005
	7·0	16·0	10·9	,,	,,	19·0	,,	1·00	0	51	0·0196	1·263	0·921
Previously reduced 10% by evaporation	3·6	16·1	13·5	29·82	759	19·5	0·738	1·00	1	24	0·0119	0·768	0·566
	4·0	16·2	13·3	,,	,,	19·5	,,	1·00	1	32	0·0109	0·703	0·518
	3·8	16·2	13·4	,,	,,	19·2	,,	1·00	1	27	0·0115	0·741	0·547
	3·8	16·2	13·4	,,	,,	19·2	,,	1·00	1	34	0·0106	0·684	0·512
Previously reduced 20% by evaporation	2·8	15·8	13·8	29·47	749	18·6	0·747	1·01	2	51·8	0·00588	0·379	0·283
	2·9	15·8	13·7	,,	,,	18·7	,,	1·00	2	52	0·00581	0·375	0·280
	3·2	15·8	13·5	,,	,,	19·0	,,	1·00	2	52	0·00581	0·375	0·280
	3·2	15·8	13·5	,,	,,	19·0	,,	1·02	3	4	0·00556	0·358	0·267
Previously reduced 30% by evaporation	2·3	15·65	14·0	30·10	765	19·2	0·757	0·50	2	37	0·00319	0·206	0·156
	2·4	15·7	13·95	,,	,,	18·7	,,	1·51	7	45	0·00325	0·210	0·159
	2·3	15·85	14·15	,,	,,	18·9	,,	0·50	2	26	0·00342	0·221	0·167
	2·3	15·8	14·1	,,	,,	18·9	,,	0·50	2	26	0·00342	0·221	0·167
	2·3	15·8	14·1	,,	,,	18·9	,,	0·50	2	34	0·00325	0·210	0·159
Previously reduced 50% by evaporation	1·5	17·3	16·2	30·13	766	21·0	0·772	1·00	8	44	0·00191	0·1231	0·0950
Previously reduced 70% by evaporation	0·2	16·15	16·0	30·40	772	19·2	0·789	0·50	6	27	0·00129	0·0832	0·0656
	0·2	16·1	16·0	,,	,,	19·2	,,	0·54	7	6	0·00127	0·0819	0·0645
Previously reduced 90% by evaporation	0·0	16·1	16·0	30·40	772	19·0	0·808	0·20	7	36	0·000439	0·0283	0·0229
	−0·6	15·4	,,	,,	,,	,,	,,	0·22	8	32	0·00043	0·0278	0·0224

curve of Fig. 7 shows the rates of evaporation plotted on a base of "fraction of petrol evaporated."

It is possible also from Fig. 6 to construct a set of curves, each at a given velocity, on a base of "fraction of petrol evaporated." This is done in Fig. 8. If the rate of evaporation is $W \frac{\text{gm.}}{\text{metre}^2 \times \text{sec.}}$, the air velocity V metres/sec. and the fraction of petrol evaporated is f, the family of curves fits an expression of the form :—

$$W = (pV + q)e^{af + bf^2 + cf^3}$$

If the petrol lies on a surface in a film of surface density 1 gm./metre^2,

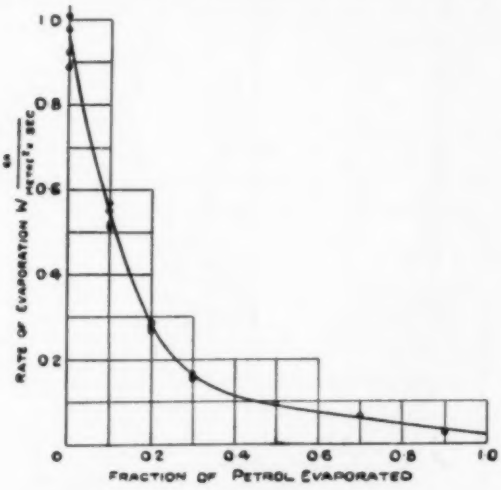


FIG. 7.

PROGRESSIVE EVAPORATION OF PETROL FILM IN STILL AIR. MEAN TEMPERATURE OF AIR, 16° C.

then the time taken to reduce it by fraction f is given by the definite integral of the reciprocal of W between zero and f. The reciprocal can be integrated graphically, and this is done in constructing the curves of Fig. 9 and Fig. 10.

For the petrol used in these tests (a good grade supplied from a garage pump) a film of 1 gm./metre^2 has a thickness of 0·000137 cm. or 0·000054 in. Fig. 10 shows that this thin film takes 13·5 seconds completely to vaporize in still air at atmospheric temperature, but half of it is gone in 2·5 seconds. Fig. 9 shows that with air blowing over it at 4 metres/sec. it completely disappears in 3 seconds, but half of it has vaporized in 0·3 second.

The time of complete evaporation is, of course, directly proportional to the film density. Thus to obtain the times to evaporate a film of a gm./metre^2 the above figures are multiplied by a.

The tests for which the figures are here given refer to temperatures

below air temperature. Since surface temperature was not capable of being controlled and maintained at any constant value, steps are being taken to provide the means of studying the effects of surface temperature in future work.

The Above Results Applied to an Engine.

Petrol leaves the jet of a carburettor chiefly in the form of drops of liquid, some of which are swept along in the air-stream. The remainder strike

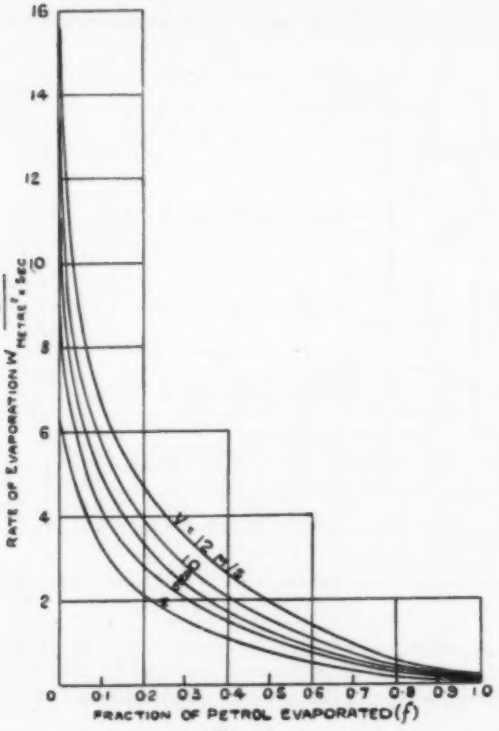


Fig. 8.

VARIATION IN RATES OF EVAPORATION AS MASS OF PETROL DECREASES.

the walls of the induction pipe and form a liquid film. The air-borne particles, if they are small, will have only a small falling speed through the air. Observations carried out by the writer on the rate of evaporation of water from spherical surfaces in still air, show that the intensity of such evaporation is a function of the diameter, the smaller the diameter the greater is the evaporation per unit of surface area.

The rate of evaporation from a plane film is, however, a function of the

air velocity; and the quantity of petrol vaporized in a given time is proportional to the area of the wetted surface.

When the jet delivering petrol into the air stream in the small vertical channel was observed, it was found that the petrol followed practically straight paths radiating outwards to form a conical spray. The outermost particles hit the walls at the level A (Fig. 11) a distance a from the jet. Let it be assumed that the spray radiates with uniform distribution, and that by the time a certain observed level B is reached (distance b from the jet) only a negligible amount of vaporization has taken place from the independent particles. Then the amount of petrol still in the

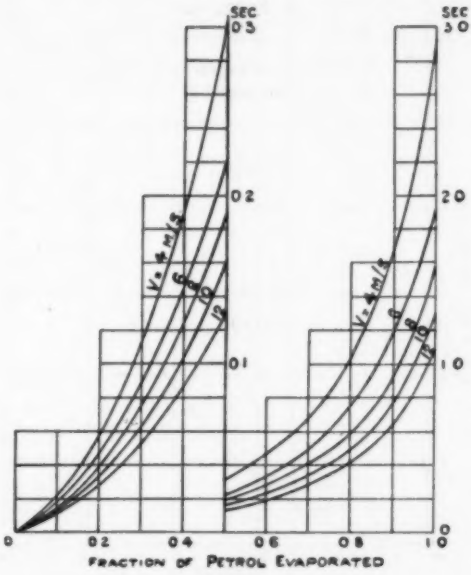


FIG. 9.

TIMES REQUIRED FOR EVAPORATING PETROL FILMS IN AN AIR CURRENT. FILM DENSITY ASSUMED TO BE 1 GRAMME/SQ. METRE; AIR TEMPERATURE, 16° C.

air-stream at B is of the total supplied by the jet. The distance a varies with the air velocity.

From the experimental data already obtained it is possible to estimate the order of the proportion of the fuel which vaporizes within a given distance from the jet, assuming that the air temperature is about 16° C.

If the distance b (Fig. 11) to the point of observation is not greater than a, then all the liquid is carried in the air stream at B in the form of particles. In this case let it be assumed that the particles are a quarter of a millimetre in diameter. For this size the limiting rate of fall through the air is less than 2 metres/sec. by Stokes' Law. Let it also be supposed (in the first instance) that the intensity of the evaporation is practically the same

as that from the plane surface as given by Fig. 6. For the fresh petrol at the given air conditions and 2 metres/sec. this rate is about

$$2{\cdot}2\ \frac{\text{gm.}}{\text{metre}^2 \times \text{sec.}}.$$

The surface area per gramme of the spherical drop is $\frac{6}{\rho d}$, where d is the diameter and ρ is the density.

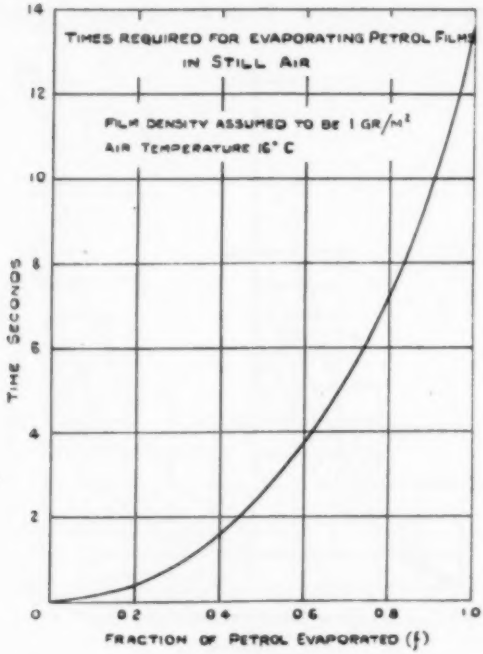


FIG. 10.

In the given case the surface per gramme is 0·0325 m.². Hence each gramme of petrol injected into the air stream loses weight at the rate of 2·2 × 0·0325 or 0·071 gm./sec.

A comparison of results obtained by the writer for the evaporation of water from the surface of a sphere in still air with values given by Hinchley (*J.S.C.I.*, 1922, **41**, 242) for evaporation from a free surface, suggests that from a surface of particles of 0·025 cm. diameter the rate of vaporization may be as high as five times that from the plane surface. Assuming that this is also true in the present case, that the air is moving at 12 metres/sec. up the vertical channel, and that the level B (Fig. 11) is 0·685 metre (27 in.) from the jet (the maximum value of b in the actual apparatus), then the amount of petrol vaporized between A and B per

gramme may be calculated thus. The relative speed of the petrol to the channel is 10 metres/sec., therefore the time from A to B is $\frac{0{\cdot}685}{10} = 0{\cdot}0685$ second. Hence the weight of petrol vaporized per gramme is $5 \times 0{\cdot}071 \times 0{\cdot}0685$ or 0·0243 gm., and in a 15 : 1 air–petrol ratio the amount vaporized per gramme of air is 0·0016 gm. If adiabatic mixing of air and petrol at 15° C. is assumed, it may be demonstrated that about 0·02 gm. of petrol, completely evaporated, would saturate 1 gm. of air. When petrol in excess of the saturation amount is present, as it is in practice, the weight of the lighter fractions evaporated would, under conditions of thermal equilibrium,

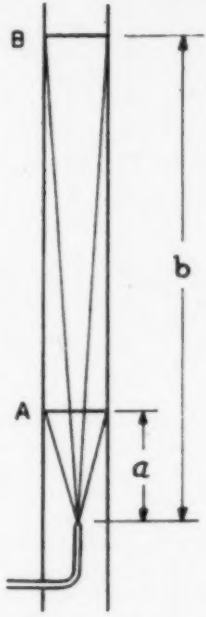


FIG. 11.

be greater than 0·02 gm. Hence less than 8 per cent. of the saturation amount is evaporated under the stated conditions.

To recapitulate, remembering that a 15 : 1 air–fuel ratio means 0·067 gm. of petrol per gramme of air, we see that only 2·4 per cent. of the petrol is actually vaporized between A and B, representing about 0·15 per cent. of the mixture.

Let us now consider the situation when the petrol is present in the induction pipe in the form of a liquid film on the surface. Let it be supposed that the film flows along the pipe with an average velocity v_p metres/sec., that the mass supplied per cm. of periphery is w gm./sec., and that the relative velocity of the air to the film is V metres/sec. It may be assumed, for the sake of this analysis, that the induction pipe is long enough to

enable the film to be reduced to nothing within its length, and that the petrol content of the air has a negligible partial pressure throughout.

The case is represented by Fig. 12. At A the petrol in its fresh condition enters the film, which at this point has a depth h cm. As it flows from A the depth of the film is reduced by evaporation, until at a point B, distant l metres from A, the depth becomes zero. The time of flow from A to B is $\frac{l}{v_p}$ sec. At A the film density is $\rho h \times 10{,}000$ gm./metre^2, where ρ gm./cm.^{3} is the density of the petrol. But $w = 100\ \rho h v_p$ gm./sec. per cm. of periphery. Hence at A the film density is $\frac{100w}{v_p}$ gm./metre^2. Now, by referring to a curve drawn for a relative velocity V metres/sec. such as is found in Fig. 9, the time t secs. for the total evaporation of a standard film (1 gm./metre^2) is obtained. The film density multiplied by t gives the time necessary for completely vaporizing the film, *i.e.* the time from A to B.

Hence $\frac{100w}{v_p}t = \frac{l}{v_p}$. Therefore $l = 100$ wt. metres, and is independent of the linear velocity of flow of the film.

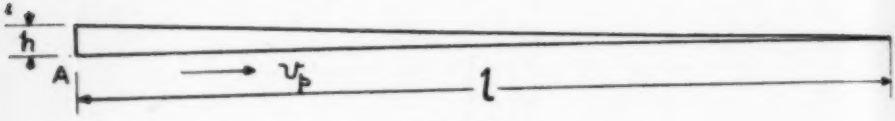


FIG. 12.

The small experimental channel used in connection with this investigation had a periphery of 20 cm., and, when dealing with a normal air–fuel ratio of 15 when the air velocity was 12 metres/sec., it received 2 gm. of petrol per second. Assuming that all the petrol was directed upon the walls, the value of w was 0·1 gm./sec. per cm. of periphery. At $V = 12$ metres/sec. Fig. 9 makes $t = 1{\cdot}1$ seconds. Hence $l = 100 \times 0{\cdot}1 \times 1{\cdot}1 = 11$ metres. Such a length would be required for complete evaporation. In practice it is, of course, possible to provide only a small fraction of this length, but we are enabled to estimate the amount of petrol evaporated at a given distance x from the jet. The time of flow over this distance is $\frac{x}{l}$ of the time of flow to the point at which the petrol disappears. The proportion of petrol evaporated at this fraction of the time required for complete evaporation can be read from the curves of Fig. 9.

In the experimental channel mentioned above, a point of observation was at 0·685 metre from the jet. Thus $\frac{x}{l} = 0{\cdot}0623$. At this proportion of the time for complete evaporation when $V = 12$ metres/sec. it is found that the fraction of petrol vaporized is only 0·08. But this is considerable compared with the 0·024 gm. vaporized when the petrol is in the form of particles (0·025 cm. diameter). Even the former figure, however, is only about one quarter of the amount of petrol required to saturate the air

at the total heat available, and it represents only 0·6 per cent. of the gaseous mixture.

Conclusion.

It seems clear that, particularly when an engine has just started, a negligible amount of the fuel enters the engine in the form of vapour. The compression stroke occupies only a small fraction of a second, and the temperature of the charge in the vicinity of the cylinder walls remains relatively low in an engine "starting from cold." Hence even at the point of ignition in such circumstances a proportion of the charge remains in the liquid state, and even when an engine is running normally, liquid particles may still persist in the charge when the spark passes. Such a state of things may well account for the notoriously variable conditions from cycle to cycle during the combustion stage in any given cylinder of a petrol engine as revealed by a modern indicator.

If all the petrol were vaporized before ignition in the cylinder, the constancy of the ignition stage would approach that of the gas engine in which the steady air–gas ratio available gives an explosion line which faithfully repeats itself from cycle to cycle when load and speed are steady.

In the above results there is evidence, on the other hand, that a high degree of vaporization in the induction is not a *sine qua non* of ignition. Ignition may, and no doubt does in a cold engine, commence from a liquid particle which comes within the high-temperature range of the spark. After all, particles of solid fuel, floating in air, may be ignited by a spark. In such a case vaporization, if it takes place, can commence only at the instant of ignition.

The results also tend to show that vaporization is most rapid when the petrol has been deposited on the sides of the induction passages in the form of a liquid film. By heating the induction passages, the vapour pressure of the film is, of course, raised, and vaporization proceeds all the more rapidly. Preheating the air alone, with the aim of increasing the rate of evaporation from air-borne particles, is likely to be much less effective, because the small relative velocity between the air and the particles makes for only a very small rate of flow of heat from the air to the particles, and therefore a very small rate of flow of vapour from the particles to the air.

In connection with the experimental observations the writer is indebted to Professor W. J. Goudie and the University of Glasgow for the use of equipment and for other facilities.

OBITUARY.

JOHN COURTENAY CLARKE, C.B.E.

We regret to announce the death, on September 29th, of Mr. John Courtenay Clarke, C.B.E. Mr. Clarke had been an Honorary Member of the Institution since 1920, and Sir John Cadman writes :—

By the death of Mr. John Courtenay Clarke, the country loses one who, after a career of faithful public service, had made his mark in the world of industry. He leaves behind him a host of business and personal friends who in his death will feel a deep sense of grievous loss.

The eldest son of the late Very Rev. John Courtenay Clarke, D.D., of Galway, Mr. Clarke was educated at Trinity College, Dublin, of which he became a gold medallist. In 1904 he entered the Admiralty Contract Department, and from 1908 was attached to the Fuel Section. In 1913 he became secretary to the Fuel Oil Committee, presided over by the First Lord, which was responsible for sending to Iran the Commission under the late Admiral Sir Edmond Slade (of which I was a member) to examine the Iranian oil-fields. Mr. Clarke was made Secretary of that Commission, whose report was responsible for the Government of the day taking a financial interest in the Anglo-Persian (now Anglo-Iranian) Oil Company.

During the greater part of the War Mr. Clarke was responsible for the purchase of fuel supplies for the fleet, and in 1917–18 he served on the Petroleum Executive as deputy director, subsequently becoming head of that organization. For his services in this connection he was made a C.B.E. In 1922 he was lent by the Admiralty to the Board of Trade as Director of the Petroleum Department, and two years later he left that post to join the Anglo-Iranian Oil Company's distribution department, a post for which his public service had peculiarly fitted him.

Among his business associates his personal qualities gained for him that esteem and affection which absolute integrity combined with generous helpfulness commands, and his intimate knowledge of the oil industry and sound judgment won for him equally high opinions from all who had business dealings with him. The sincere sympathy of a wide circle of friends is, I feel sure, extended to Mrs. Clarke and her son in their bereavement.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Forty-eighth General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on April 29th, 1936, Commander H. V. Lavington, R.N., Branch Chairman, in the Chair.

The following paper was read :

THE PERFORMANCE, ETC. OF DIRECT GAS-ACTUATED PLUNGER UNITS.

By G. A. WALLING, B.Sc. (Associate Member).

SYNOPSIS.

The purpose of the paper is to give details of scope and performance of several plunger lifts under various field conditions. An outstanding feature of the system is its somewhat unique method of utilizing available formational energy.

An installation consists of a steel plunger travelling back and forth in a special string of tubing, carrying oil to the surface in its upward travel and allowing the lifting gas to be exhausted during its return. The energy for operation may be entirely supplied from the formation, or, if this is insufficient, additional gas may be admitted to the casing from some surface supply.

Very deep wells have been produced by this method, and also a wide range in the capacity of the units has been demonstrated. Both heavy and light oils have been successfully produced.

The wear on equipment appears to be confined to the plunger, and is governed principally by the abrasive condition of sediment entering the flow string.

Lifting costs are very low where sufficient formational gas is available to make the units self-sustaining. Under these conditions the costs are comparable with those of flowing wells.

INTRODUCTION.

Recent developments in production practice have resulted in a wide range of methods being available for artificially raising oil from the producing zone to the surface. Among the many systems now being employed in various fields is the gas-actuated plunger pump, more commonly known as " Plunger Lift," which utilizes the energy of the formational gas in a somewhat unique manner.

The introduction of any system which fully exploits the formational gas energy during the close and subsequent to the close of the flowing life of a well has obvious and attractive possibilities from the theoretical point of view. The decision as regards its installation will depend on its ability to operate economically for long periods, also on its range of application under varying field conditions.

The purpose of this paper is to give some details of the scope and performance of several plunger-lift units under various conditions.

Operation of System.

Briefly, an installation consists of a string of tubing manufactured to closer limits than standard (the tolerance allowed being $\pm$ 0·01 in.). This flow string may be considered the working barrel of the pump. A steel plunger travels back and forth from top to bottom of the flow string. In its downward travel the plunger passes with its valve open through fluid in the lower part of the tubing, until reaching the foot-piece, where the valve is automatically closed on to its seat. Gas pressure from the casing then elevates the plunger to the top of the flow string with a slug of oil above it and discharges the fluid through a choke. At the top of its stroke the plunger, together with a small portion of lifted fluid, runs into a chamber, where the valve is pushed off its seat by the dead fluid above it allowing the gas below to exhaust through the plunger as the latter returns to the foot-piece at the lower end of the flow string.

By means of the choke on the discharge of the flow string the rate of production of the well may be controlled in similar fashion to any normal flowing well. Also it serves to check the release of the lifting gas as the plunger is falling to bottom. Too high a gas velocity through the flow string during this period will blow the valve of the plunger up on to its seat, resulting in the plunger returning to the surface before having reached the foot-piece at the lower end of the flow string.

The gas energy for operating the plunger may be either supplied solely by the gas entering the well with the crude from the formation or, if this is insufficient, additional gas may be admitted to the casing from some surface supply. It will be appreciated from the above outline of operation that there is a pressure in the annular space between the casing and tubing throughout the operation.

The volume of gas required for lifting purposes is directly proportional to the length of the flow string or working barrel for any given rate of production.

Other factors which affect the lifting ratio to a lesser extent are :—

(i) Degree of back pressure carried at well head.
(ii) Design of plunger.
(iii) Physical properties of fluid.

Increasing the well-head back pressure will raise the volume of gas required for lifting a given volume of fluid. The design of the plunger affects its falling speed, and during the period of descent an interval ensues when no useful work is being done. Any reduction of this period by streamlining the plunger and reducing frictional resistance will lower the gas volume required for lifting purposes.

For example, in a well producing 50 barrels per day from a depth of 3500 ft. the plunger was replaced by one of improved design. Without any other change in operating conditions the number of cycles increased from 10 per hour to 11$\frac{1}{2}$ per hour, and it was possible to reduce the overall gas consumption by approximately 15 per cent.

The physical characteristics of the crude, such as viscosity, B.S. content, and gravity, affect the resistance to travel of the plunger, and therefore have some effect on the gas energy required for operation.

In general, the average volume of gas required for operation is 500 cu. ft. per 1000 ft. of lift per barrel of fluid lifted. Due to the factors outlined above, the volume required in practice may be somewhat higher or lower. However, it may be taken as a useful guide in predicting the performance of any well where production data are available as to gas–oil ratios prior to the application of the system.

Application and Capacity.

Since the equipment requires the maintenance of some pressure in the annular space between the casing and working barrel, it is necessary that the crude can enter the foot of the hole against some back pressure throughout the life of the well, in order that this system may produce the well to the point of abandonment.

These conditions exist in many medium-depth or deep formations, where comparatively tight sands and high fluid level conditions are prevalent, for the operating pressure is always below the critical back pressure at which maximum production can be obtained.

In producing strata where very porous sands having a high productivity factor for a low formation pressure have to be exploited, the system could be utilized as an intermediate stage between the flowing period and the final stage where all back pressure has to be removed from the sand-face in order to recover production.

The maximum lifting capacity of the equipment is controlled by the working pressure, the diameter of the working barrel and also its depth. The greatest production so far handled is reported from the Oklahoma City field, where a 4-inch unit delivered approximately 1020 barrels per day from around 6400 ft., with a casing pressure of 262 lbs. per sq. inch. One of the smallest wells on record was located in Texas, and produced 8 barrels per day from a depth of 3400 ft. with a casing pressure of 8 lbs. per sq. inch. A 2½-inch flow string was used in this well.

One of the deepest wells operated by the system is situated in the Ventura Avenue field, California, and is equipped with a 2¼-inch working barrel with the foot-piece set at 6800 ft., approximately at the bottom of the hole. The production has averaged 150 barrels per day with a casing pressure of 180 lbs. per sq. inch.

The oils that have been pumped over a relatively wide range of gravity as well as viscosity. The heaviest oil of which the writer has knowledge had a specific gravity of 0·964 at 60° F. and an absolute viscosity of 6·4 poises at 100° F., this being from one of the wells in the Maracaibo Area. The lightest oil so far produced has been obtained in Texas, having a gravity of 0·791 at 60° F. and an absolute viscosity of 0·0123 poise at 100° F.

Paraffinic crudes seems to offer no obstacle to the application of the system. A well in the Palo Seco Field, Trinidad, is being produced from a depth of 4200 ft. and yielding oil with a solidifying temperature of 65° F. The plunger occasionally hangs up in the flow string whenever the night temperature falls below normal.

The standard clearance of 0·02 to 0·03 inch between the plunger and working barrel is quite satisfactory for use with the lighter oils, but it has been found that it is necessary to provide somewhat larger clearance for

use with the more viscous oils, in order to permit the plunger to return to bottom with a reasonable lapse of time. With oils similar to the heavy Venezuela crudes, it has been found that a clearance of about 0·04 to 0·06 inch is very satisfactory.

As regards the ability of the system to handle formation, it has been found that relatively large quantities of sand can be produced. One well of which the writer has record produced approximately 20 barrels of sand in one day for a production of 240 barrels of oil. In the Palo Seco field, Trinidad, the system has been applied to wells in which formational mud and sand are present in varying quantities. Toward the close of the life of the wells this difficulty often increases, and the B.S. enters the holes at low rates of oil production. As long as the mud–sand mixture is soft in character it has been produced with very little trouble. In cases where harder shale has been present, frequent shut-downs have occurred through the plunger failing to return to bottom.

Recently, the system has been modified to cope with low-pressure porous sand conditions. But the installation is still in the experimental stage. A chamber is carried below the foot-piece of the flow string, and surface gas is the sole medium for lifting the crude.

This is supplied through a macaroni string, while the formational gas is released to atmosphere through the casing. No data are yet available as to how the surface energy required for operation compares with other systems.

Maintenance and Wear.

The most common trouble experienced in the Palo Seco field has been the failure of the plunger to return to the foot-piece on account of hanging up in an accumulation of either mud, sand or paraffin wax. In this position, the valve in the plunger is open, and the gas pressure cannot build up below the plunger to elevate it to the surface. Almost invariably it may be recovered by an operator dropping a fishing tool " into the " plunger, which allows pressure to be built up on the casing, and the plunger blown to the surface. Should this fail, a small spear may be lowered on a sand line run from a winch.

Sometimes the severity of the B.S. condition is only temporary. For example, conversion from flowing or straight gas-lift status may result in an increased production rate with a large initial amount of formation mud, etc. The temporary use of a well-worn plunger and a liberal supply of input gas will reduce the initial difficulty of obtaining proper operation. Later the plunger may be replaced by one of full dimensions and the gas consumption reduced.

Another less frequent source of shut-down is the failure of the valve in the plunger to be pushed off its seat at the top of its travel on account of the plunger valve-cage becoming plugged with sand or mud. This trouble may be reduced to a minimum by filing small notches in the valve-seat. This allows a small quantity of the lifting gas to leak through the plunger and keep the sand in suspension in the slug of oil above the plunger, instead of settling back into the latter.

By placing a chamber, constructed from scrap casing, between the flow-head and discharge choke of sufficient volume to receive each slug of oil,

the upward velocity of the plunger will not be checked, as in the usual installation, where the plunger cannot reach the surface until the oil has been discharged through the control choke. This helps to prevent the B.S. from settling back in the plunger.

Wear of the equipment is confined almost entirely to the plunger. After nearly two years' operation from a depth of 3450 ft., the flow string of a 2-inch unit in the Palo Seco field shows no measurable sign of wear, and continues to function without any apparent loss of efficiency. Table I

TABLE I.

Plunger Wear.

Well No.	Operating Period, months.	Original Diam., inches.	Final Wear Diam. at Top, inches.	Final Wear Diam. at Middle, inches.	Final Wear Diam. at Base, inches.	Total Mileage.	Max. Deviation of Hole.	B.S. Condition.	Remarks.
1	5½	2·032	2·015	2·014	2·002	76,000	3°	Very slight, 0·1–0·2%	A rebuilt plunger still operating.
2	4½	2·035	2·000	1·970	1·930	61,000	17°	Variable 0·5–1·5%.	Originally new. Removed for rebuilding.
3	6	2·035	2·030	2·029	2·010	78,000	2½°	Very slight, 0·1–0·2%.	Originally new. Still operating.
4	4½	2·480	2·44	2·404	2·375	50,000	2½°	0·3–0·6%.	Originally new. Removed for rebuilding.
5	5	2·035	2·007	1·970	1·950	61,000	8°	Variable, 0·5–1·5%.	Originally new. Removed for rebuilding.
6	1	2·035	2·016	2·000	1·997	12,000	9°	Variable, 0·8–4%.	Very little more life.

shows the record of the life of the plungers in various units. The length of life appears to be dependent on the following factors in order of their influence :—

(i) Amount and degree of abrasive quality of B.S. lifted.
(ii) Volume of fluid lifted per cycle.
(iii) Mileage per day.
(iv) Deviation of hole.

In those wells where considerable deviation exists, the plungers show maximum wear on one side, indicating that they do not rotate in their travel. Except for wearing the plunger in a more eccentric manner, deviation has very little effect on the life.

There is some degree of uniformity of production rates, etc., of the various units mentioned, and therefore the effect of the volume per cycle on wear is based on the writer's observation of larger wells which have been producing for too short a period to present any accurate data. Practically no wear takes place on the valve-face or valve-seat, but the length of the valve-stem gradually shortens. However, this will not affect proper operation for a considerable period.

In the cases where the plungers have had to be removed, the recording charts show a slowing up in the number of cycles per hour a few days prior to stoppage. Unless the gas supply is increased, the plungers eventually remain at the foot of the flow string.

It has been found possible to restore worn plungers to their original diameter quite cheaply by means of deposition of metal. Good-quality bronze has been used with successful results. However, there is no reason why other metals should not yield even longer life.

In the case of Well No. 6, the rate of wear has been exceptionally high, on account of the extremely abrasive nature of the sand produced. However, this was anticipated, as other methods of production had also shown extremely rapid wear on the equipment involving many work-over jobs.

Table II gives data relative to the production expenses of eight wells in Palo Seco.

TABLE II.

Lifting Costs.

Well No.	Operating Period, months.	Total Production, barrels.	Cost per Barrel, cents.	No. of Times Worked Over after Installing.	Reason.
1	7	6,736	6·8	Nil	—
2	7	8,172	7·7	1	To lower tubing 210 ft.
3	7	10,368	4·3	Nil	—
4	8	8,037	7·6	1	To clear foot-piece of mud and bail.
5	17	21,585	6·2	3	Once to instal tail-pipe. Twice to bail-hole.
6	2	2,693	15·2	3	Trouble with plunger sticking at bottom of tubing. Eventually located trouble. Collapsed casing buckled bottom three joints.
7	1	2,418	5·5	Nil	—
8	6	4,606	10·1	1	To change foot-piece stop.

The following items have been included in this statement :—

(i) Supplies.
(ii) Cleaning.
(iii) Transport.
(iv) Travelling.
(v) Labour.
(vi) High-pressure gas expense.
(vii) Maintenance of roads and derricks.
(viii) Depreciation.

The cost of installation and of superintendence are not included. Each flow string or working barrel has been depreciated over a period of eight years. The remainder of the equipment has been depreciated over a period of five years.

The wells enumerated in this schedule include those listed in Table I. The comparatively high lifting costs of Well No. 6 were due to the bad mechanical condition of the hole. Over a longer period the expense should decrease, as since the initial difficulties were overcome no operating trouble has been experienced other than occasional stoppages due to the severe B.S. conditions, and these stoppages have been rectified by one trained native operator.

In Table III are set forth general production data of the wells under review. It will be noted that six of the units are self-sustaining, while a small quantity of surface gas drawn from high-pressure flowing wells is used to operate the others.

TABLE III.

General Production Data.

Well No.	Depth, feet.	Tubing.		Average Daily Production, barrels.	Specific Gravity.	Casing Pressure, lb./sq. in.	Tubing Pressure, lb./sq. in.	Volume of Fluid/Cycle, barrels.	Input Gas Ratio, cu. ft./bri.	Output Gas Ratio, cu. ft./bri.	Remarks.
		Depth, feet.	Size, ins.								
1	3190	2804	(2)	32	0·858	35	5–17	0·074	—	5487	Self-operating. Some gas bled from casing.
2	3300	2889	(2)	30	0·877	45	6–25	0·095	—	2914	Self-operating.
3	3400	3203	(2)	30	0·884	75	10–50	0·125	—	2800	Self-operating.
4	3259	3030	(2½)	33	0·902	30	10–25	0·114	—	4000	Self-operating.
5	3700	3450	(2)	42	0·883	50	5–30	0·135	730	2400	—
6	3480	3160	(2)	45	0·888	50	5–35	0·145	956	2600	—
7	3610	3500	(2½)	80	0·868	70	10–50	0·255	—	2400	Self-operating.
8	2620	2000	(2)	26	0·875	30	6–20	0·052	—	?	Self-operating.

The average overall lifting cost from the eight wells under review has been 7·0 cents per barrel for a fairly long period. Of this amount the direct cost, excluding depreciation of equipment, was 2·5 cents per barrel.

The author's thanks are due to the Directors of the Trinidad Petroleum Development Company for permission to publish this paper.

DISCUSSION.

MR. J. D. FULLERTON quoted the author's statement under the sub-head "Operation of System," and stated that in their notes the makers, like the author, also claimed that the valve was pushed off its seat by meeting the stationary slug of oil in the stack at the top of the stroke, but from personal observation he could not agree with this. He said that, in his opinion, the valve opened by gravity, and that this was clearly demonstrated by opening the by-pass, together with the usual outlet. The pressure below and above the plunger was thus equalized, but no difference in the cycle was noted.

In practice the valve would open irrespective of whether the slug of oil was held in the stack or not.

In the second paragraph the author stated that "by means of the choke on the discharge of the flow string the rate of production of the well may be controlled in similar fashion to any normal flowing well." In the speaker's experience that was applicable only within narrow limits. There were many cases where a reduction in the outlet choke would increase the production (which was the converse of the normal well flowing practice) merely on account of accelerating the falling speed of the plunger.

The author had also referred to the "degree of back pressure carried at the well-head" as one of the factors affecting the lifting ratio to a lesser extent. The speaker desired to know whether that was casing pressure, back pressure at the time of the plunger striking bottom, or the minimum tubing pressure recorded.

He also asked the author, if possible, to let him have any further information on designs of plungers. He, personally, had had experience of only two types—Type W.7 and the "Speed Type."

With regard to the average gas/oil ratio of 500 cu. ft. per barrel per 1000 ft. of lift, they had not devised any satisfactory means of measuring

the output accurately. The input was comparatively simple. In the maker's original notes, however, is given a statement of results obtained from a number of wells, and in some cases the gas/oil ratio was 1000 cu. ft. per barrel. In one particular case the input gas gave a ratio of 620 cu. ft. per barrel. It seemed, therefore, that there was a big variation in those ratios, depending on the characteristics of the well.

In connection with streamlining the plunger, and so reducing the frictional resistance, he thought that this could be achieved comparatively easily, but it was his view that the limit of falling speed must be governed by the ability of the valve stem and cushion seat to withstand the force of the impact. There must obviously be a limit beyond which it was unsafe to go—just what that limit was he did not know, and would like to hear the author's views thereon.

Mr. K. W. G. Patterson opened his remarks by alluding to the same paragraph with regard to the control of production with the surface choke. It had been found by experiment on the field that the control of production by this means was very limited. In two cases a liberal increase of the choke had not resulted in any increase in production. However, under the conditions to which Mr. Walling referred later—*i.e.*, where the critical back pressure due to sand conditions was in excess of the back pressure applied—these results were to be expected.

Another factor which he considered of importance in the control of production was the volume of gas which it was necessary to produce with the oil.

In the circumstances in which the gas/oil ratio was considerably in excess of that actually necessary to lift the oil to the surface, the main purpose of choking the well was to prevent short stroking of the plunger. Also the volume of gas which had to be liberated after each stroke had some effect in the back pressure. It would be realized that when the plunger reached the top of its stroke, the entire length of the tubing was filled with gas at the maximum discharge pressure, and that this volume of gas had to be released in order to reduce the back pressure at the foot-piece.

He considered it probable that the volume of gas being produced through the tubing in excess of practical requirements was really a hindrance to the production of oil. Experiments were in progress to bleed off this excess gas from the casing.

A theoretical figure of 500 cu. ft. per barrel per 100 ft. of lift had been given as the volume required to operate the plunger.

He had taken some notes at random from their production data to show the ratios being obtained as compared with the above figure, and also in relation to the barrels of oil being lifted per pound per square inch of casing pressure.

With the 2-inch outfits the figures obtained were as follows :—

Gas/Oil Ratio per 1000 Ft. of Lift.	Barrels Lifted per Lb. per Sq. Inch Casing Pressure.
1400	0·70
1140	0·47
1130	0·50
1100	0·70
1000	0·91

With 2½-inch Outfits:

Gas/Oil Ratio per 1000 Ft. of Lift.	Barrels Lifted per Lb. per Sq. Inch Casing Pressure.
1130	0·5
1000	0·96
1000	0·71
720	1·25
690	1·25
650	1·24

It could be seen that all these ratios were in excess of the theoretical figure. With the 2-inch outfits, the ratios cited happened to be about the same, and no particular relation could be observed.

With the examples given for the 2½-inch outfits the tendency for the barrels lifted per unit of casing pressure to increase with the decrease in lifting ratio was more clear. This showed that the amount of back pressure being held on the well was due to some extent to the volume of gas being produced.

He thought that an interesting example could be given from the data on one well, which in the earlier stages had a lifting ratio of 1700 and was lifting 0·6 barrel per lb. per square inch casing pressure. The gas production later declined when the lifting ratio was reduced to 690 and the barrels lifted increased to 1·25. The oil production in both instances was the same.

In regard to the question of maintenance, a small point not mentioned in the paper was the trouble experienced due to the bending of valve spindles.

He did not think, as Mr. Fullerton had remarked, that this damage could be due to high falling velocities, but to the plunger striking the foot-piece slightly off centre. He knew of one well in which the plunger had been operating for several months with an average falling velocity of 100 feet per second, or over 60 miles per hour, without any bending of the valve spindle occurring. On the other hand, in another well in which the falling velocity was much less, but in which the hole was known to be crooked, the valve spindle had been bent repeatedly.

The author had mentioned paraffin wax as one cause of trouble in plunger operation, and he thought that in this connection heating of the input gas would prove beneficial. He had had an interesting experience recently when attempting to kick off a well in which the plunger had been held up in the tubing. Pressure was first built up to 500 lbs. per sq. inch through the ordinary kick-off system, without success. A portable compressor was then moved up to the location and connected direct to the casing-head. In this case the well kicked off after a pressure of 370 lbs. per sq. inch had been built up. This was presumably due to the hot air discharged by the compressor raising the temperature of the fluid and loosing the paraffin deposit.

Mr. H. C. H. Darley inquired of the author if he had any way of finding the correct tubing depth beyond the usual method of trial and error. To get the most efficient cycle it was necessary to get the correct tubing depth. This would result in a saving of gas.

He agreed with the last speaker with regard to the question of input gas and the correct ratio of chokes, as too much gas resulted in inefficiency and

an irregular cycle. He found a very good check on performance was by balancing casing pressure against total load. The total load could be arrived at by selecting any convenient point on the cycle, usually when the top of the slug reached the output choke. The total load is then the pressure above the slug, plus the amount of oil above the plunger plus an allowance on a time basis for the oil that will have collected in the bottom of the tubing since the plunger left bottom, plus the weight of the plunger, and 20 per cent. was usually allowed for friction. This figure expressed in lbs. per sq. in. is then subtracted from the casing pressure, and the difference might be called "excess pressure." It should be approximately a constant for wells of the same diameter tubing. He had found that wells with a low excess pressure were liable to quit easily and to give irregular cycling, while those with a high excess pressure would give short stroking or a high gas/oil ratio. To alter the excess pressure it was necessary to alter the ratio of input to output choke. For instance, to increase it, it would be necessary either to open the input choke or close down on the output choke, or both, according to other conditions in the well.

Another point on which he desired some information from the author was his reference to putting a chamber between the flow-head and the discharge choke. He would like to know what effect this had on the general cycle apart from the effect on the B.S. On the face of it, it seemed that it should increase the efficiency of the cycle and give a reduction on input gas/oil ratio.

Mr. A. J. Ruthven Murray said that the author had referred to his experience in Maracaibo with wells operating on plunger lift handling heavy oil of sp. gr. 0·964. He would like to know whether large- or small-size tubing was used in such wells. Apparently the author had experience of a wide range of tubing, as, in the paper, he referred to tubing as large as 4 inch and as small as 2 inch. Perhaps he could tell them which size of tubing was likely to be more suitable with heavy viscous oil.

Mr. Ruthven Murray said he understood that, when plunger units were first introduced, the tubing was reamed; but that cold-rolled tubing was now used. The author had made no reference to the two types of tubing, and the speaker wondered whether there was much difference in performance or cost; he presumed the cold-rolled would have a greater tolerance.

Mr. R. Godfrey said, with reference to a point raised by a previous speaker, relating to the bending of valve spindles, he thought that the density of the gas and oil column at the bottom of the working barrel or just above the foot-piece had a great deal to do with it. This could be controlled to a large extent by beaning and bleeding off excess gas from the casing. Too long a tail-pipe would also reduce the density of the gas and oil mixture at the foot-piece itself.

With reference to the paraffin well referred to in the paper; in nine cases out of ten the stoppages had been due to short stroking, and not due to the plunger hanging up in the working barrel. The type of plunger used in this particular well employed a tapered valve-stem, as distinct from the other type of plunger which employs a straight valve-stem.

His theory was that the high viscosity of the oil held the valve off the

taper in the valve-cage, and caused it to be blown back on to its seat before the plunger got to the foot-piece. This being the case, the use of a plunger which employs a valve having a straight stem should overcome this difficulty.

MR. J. S. OGILVIE inquired of the author if the Hughes plunger had been successful in all wells in which it had been tried, provided the mechanical condition of the well was good.

MR. A. H. RICHARD said that the author had referred to the opening of the valve at the top of the stroke as being due to dead oil above it. Mr. Fullerton had queried that, and he agreed with Mr. Fullerton's query. It was possible, as demonstrated by the model, that with a slow rising stroke and dead oil above the plunger the valve would not open, and the plunger would stay at the top. He was inclined to think that the only thing that would open the valve was a sudden reversal of the plunger after a quick rise, the valve being more or less shaken off its seat.

The author had spoken about putting a chamber between the outlet and choke. In connection with that he would like to ask the author what he did with the gas which was exhausted from the flow-string—whether he collected it, or made use of it in any way. It was standard practice with his Company to install a separator at each plunger-lift well and collect the gas which was either re-cycled to the absorption plant or piped to fuel supply as the case might be. He believed the ideal arrangement would be to install the separator before the choke, thus combining the two systems.

MR. G. A. WALLING, in reply to the discussion, said Mr. Fullerton had raised the question of the valve opening when the plunger reached the top of its travel. The author had reached the conclusion that the valve was pushed off its seat by the pressure of fluid trapped in the flow-stack above the plunger from field observations. Not only was the valve opened by this fluid, but the plunger was checked in its upward travel by the same resistance. Whenever the plunger reached the surface with no fluid above it, due to short-stroking or some other cause, the plunger was only checked in its upward travel by the safety bumper at the top of the flow string, where it remained until removed. By placing a pressure gauge on the flow stack he had determined that the initial pressure created at this point was greater than the discharge pressure, thus resulting in a downward pressure on the plunger and valve. The excess of pressure above the plunger at the instant of its arrival in the flow stack had been observed to bear a direct relation to its upward velocity. Mr. Richards had mentioned that it could be demonstrated by the working model that when the plunger rose slowly, the valve very often remained closed and the plunger remained at the top of its stroke. In the author's opinion this confirmed the field observation just mentioned, and that the flow-stack pressure was not sufficiently in excess of the pressure beneath the valve to give a large enough downward resultant to open the latter.

As regards the ability to control production rates by means of varying the discharge choke area, it should be remembered that the degree of response to changes in choke size was fundamentally related to the produc-

ing characteristics of the formation. For example, where production was being obtained from a tight sand, the operating pressure of the unit might be reduced by increasing the choke size without any response as regards increasing the production rate, on account of the fact that the general operating pressures were already below the critical back pressure permitting maximum rate of production. However, decreasing the choke area must ultimately cause the general operating pressure to reach a point above the critical back pressure, and be responsible for a reduction in producing rate. The change would be dependent on the productivity factor of the particular formation. Plunger units were being operated in some fields in the States where proration was in force, and the individual well productions were kept within restricted limits by means of surface choke control.

As regards the limiting falling speed which could be attained by change in design of the plunger, he had not yet obtained data to show exactly what was the safe limit. In Well No. 4 in Table I of the paper an exceptionally high falling speed had been obtained. It had averaged about 100 ft. per second, and yet no trouble had been experienced from damage to valve or cushioned seat. On the other hand, units operating in wells of similar depth with a slower falling speed had given trouble occasionally with bent valve spindles. A survey of such wells had always shown them to be crooked. Theoretically, this should have no influence on the trouble experienced.

One method of determining the volume of output gas was to record the differential head registered on a standard orifice meter at short equal intervals of, say, 10 seconds, and compute the average rate of flow per cycle from this data. By assuming no variation in the delivery per cycle, the daily output volume of gas could be determined. Where regular operation was being obtained very little error was incurred by making this assumption.

Mention had been made that lifting ratios in practice varied considerably and were very often in excess of the estimated required quantity of 500 cu. ft. per barrel per 1000 ft. of lift. This was very often due to the natural formational ratio being in excess of lifting requirements. Or again, it might be due to the amount of choking at the well-head. Assuming all other factors equal, a reduced choke area increased the general operating pressures, *i.e.* casing, minimum tubing pressure and pressure at the time of the plunger striking bottom. Where only the minimum amount of gas had been available for lifting purposes, it would be found that this minimum amount would ultimately have to be increased when operating pressures were raised by choking back the discharge.

Mr. Darley asked how the tubing depth had been determined. In all those wells under review in the paper it would be found that the volume lifted per cycle was very small and their general production was low. In all these cases the only limit to the depth of the flow strings was governed by factors other than any relating to correct operation of units.

In comparatively large producing wells too great a submergence of the flow string would result in a straight gas-lift operation super-imposed on the discharge by the plunger, and the only way to minimize that would be by trial and error.

The placing of a chamber between the flow-head and discharge choke improved the operating efficiency in large wells. It enabled the plunge

cycle of travel to be reduced, for no delay occurred at the top of its stroke, as the delivery of the slug was almost instantaneous. Thus the percentage of useful working period to the overall period of the cycle was increased. However, in the case of small wells, the time taken to discharge a slug direct through a choke was so small that no practical saving as regards lifting efficiency was obtained by the use of a chamber.

As regards the success or failure of units sought by Mr. Ogilvie, an instance had occurred in the Palo Seco field, where the steady operation of a unit on a deep well had been frequently interrupted by the entry of shale mud into the flow string. In this particular case the fluid level rose rapidly after a shut-down, and an exceedingly high pressure was required to restart flow. The inconvenience caused to other field operations made it desirable to move the unit to a more favourable location.

On the question of tubing tolerances raised by Mr. Ruthven Murray, in the early days of development, the manufacturers of the system worked over ordinary tubing which involved reaming. Later the pipe mills had been able to supply cold-drawn tubing to within the tolerances required. There was practically no difference in the actual limits of the old style tubing and the tubing now obtained from the wells. Originally the tolerance allowed was + 0·01 inch — 0·005 inch, while cold-drawn tubing had a tolerance of ± 0·01 inch. As a result there was no difference in performance but the cost was reduced.

To produce heavy oil from wells in the Maracaibo district 2½-inch and 3-inch flow strings have been used for rates of production varying from 90 to 220 barrels per day. The choice of tubing diameter would be governed by the production to be lifted. In any case, the 2½-inch flow string was preferable to the 2-inch size, provided the casing diameter permitted it.

With regard to Mr. Richard's query as to the disposal of gas production, it has always been the practice of the author's company to deliver the gas to a light products recovery plant whenever the presence of light ends was proved to exist in commercial quantities. Wherever operations justified the installation of a separator at each individual well it would be possible to dispense with the chamber hook-up outlined in the paper, provided the separator would withstand the maximum well-head discharge pressures and was not too large in capacity. Too large a separator would allow the initial gas flow following each oil slug to be maintained at a comparatively high discharge velocity before the choke on the discharge of the trap could affect the cycle. This might cause the plunger to short-stroke before its return to the foot-piece.

On the Chairman's proposal, a very hearty vote of thanks was accorded the author for his paper, and to the President and Members of the Apex Club for the use of their rooms.

THE HARD-FACING OF OIL-WELL TOOLS.*

By E. W. Bentley.

Tools used in the drilling of oil wells must of necessity be subjected to severe conditions of wear, due to the nature of the formations encountered during the drilling operation.

Well-head equipment also, operating under the strain of the rotary movement and the running of tons of drill pipe in and out of the hole, is liable to considerable depreciation.

A great deal of the drilling time is lost in pulling out of the hole to replace worn drilling tools and running the new tool into the hole again. Therefore the longer period that the drilling tool can be kept on bottom and operate satisfactorily, the less round trips are required, with the result that there is an all-round saving on drilling equipment.

With the object of prolonging the life of the cutting tools in the hole, various methods of treating the tools have been introduced into the oil-well drilling industry.

These methods are known as "hard-facing," and the materials used in hard-facing drilling tools are applied by welding. Hard-facing materials, although highly resistant to abrasion, are as a rule of a hard and brittle nature, and require the "backing" of some other stronger material to become efficient in operation. Therefore hard-facing is, as the name implies, a surfacing operation.

Even with the use of hard-facing materials, however, it is not possible to present excessive wear of the drilling tools, and in practically all cases it is necessary to "build up" or weld the tools to the original shape and size prior to hard-facing.

In building up and hard-facing, both the oxy-acetylene and electric arc methods of welding can be utilized, and it is a matter of discrimination on the part of the welder-in-charge as to which method is the more suitable for application to the class of work which it is required to repair. Also, the same type of welding or hard-facing material is not suited to all work, and it is necessary to decide which material is best to use for the particular work or job in hand. The most commonly used hard-facing materials at the present time are :—

(*a*) "Stellite," and the process of hard-facing is known as stelliting.
(*b*) Tungsten carbide inserts.
(*c*) Tungsten carbide in powder form.
(*d*) Composite rods.

Dealing with (*a*), Stellite is a non-ferrous alloy, and is composed of cobalt, chromium and tungsten. It is manufactured in the form of rods 8 to 10 inches long, and can be deposited by either the oxy-acetylene or the electric arc methods of welding. Stelliting by the oxy-acetylene method is the easier and more economical of the two. This would scarcely

* Paper read before the Burma Branch of the Institution of Petroleum Technologists, March 13th, 1936.

be thought possible, as the cost of oxygen and acetylene is higher than that of electricity. During the operation of hard-facing with Stellite by the electric arc process there is a considerable loss of Stellite due to volatilization and the spluttering action which takes places under the arc. It has been found by accurate test that the loss in Stellite under the action of the arc is as high as 12 per cent. Also, owing to the extent to which penetration of the parent metal takes place, the deposited Stellite is liable to become diluted with the softer metal of the tool, thereby lowering the efficiency of its resistance to abrasive action. It is practically impossible with the electric arc to deposit Stellite in such a manner as to leave clean sharp edges, and as drilling tools must be sharp and finished to gauge size, an excessive amount of grinding is often necessary in order to obtain the desired results. No loss of Stellite is incurred when using the oxy-acetylene method, and it is possible to obtain a smooth deposit and to leave cutting edges sharp and finished to size without the further operation of grinding.

(*b*) Tungsten carbide is not a weldable metal. It is believed to be an alloy of tungsten, carbon and cobalt. It varies in hardness from 1200 to 2500 Brinell. When used in insert form for hard-facing it usually requires a covering of some other material to hold the insert in position. The procedure most commonly used is to place the inserts at intervals along the faces or cutting edges of the drilling tools, afterwards covering the whole with Stellite. In this case also the most suitable method of application is by the oxy-acetylene flame. Under the action of the electric arc or the oxy-acetylene flame, tungsten carbide does not reach a molten condition, but slowly oxidizes. This reaction is brought about to a greater extent by the electric arc, and in all probability affects the structure of the parent steel. The high temperature of the arc is also liable to cause cracking of the tungsten carbide inserts. The same conditions for stelliting over the inserts apply as for stelliting, already described.

(*c*) Tungsten carbide in powder form. This is a modified form of tungsten carbide, and is known by various trade names, such as Blackor, Britor, Griffiner, etc. It is composed of tungsten and carbon. Hard-facing with tungsten carbide in this form can only be successfully undertaken by the electric arc process, as an extremely high temperature is required for its application. Also, being in the form of powder, it is not suitable for application by the oxy-acetylene method, as the force of the blowpipe flame tends to blow the powder from the work. In combination with the carbon arc, which acts somewhat in the manner of the electric crucible, the tungsten and carbon powder changes its form to tungsten carbide on the face of the tool to which it is applied.

(*d*) Composite rod is an improved form of hard-facing with tungsten carbide, and is intended to replace the method of using large tungsten carbide inserts. The tungsten carbide is crushed to granular form in varying sizes from coarse to very fine particles, and then formed into rods by placing the particles in a mould or shape, and with the oxy-acetylene flame binding the particles together with a low carbon-steel welding rod. Composite rod is also formed of crushed tungsten carbide, using Stellite as a binding material. The percentage of tungsten carbide contained in the rod varies according to the amount it is desired to place on

the work which requires hard-facing. The most suitable method of application in this case also is the oxy-acetylene flame.

Fish-Tail Bits.

The fish-tail bit is probably the most widely used tool in rotary drilling; at least, it was until a short time ago. All the hard-facing materials which have been described can be used on this type of drilling tool.

We will take the method of stelliting first, as I believe this was the first type of hard-facing used.

The fish-tail bit is first dressed to gauge in the blacksmith's shop, and afterwards stellited in the welding shop. Stelliting as a rule requires that the work to be hard-faced should be preheated and cooled slowly, as Stellite after deposit is very liable to checking or cracks, due to uneven contraction in cooling. In the case of fish-tail bits, however, preheating is not absolutely essential, as the heat of the oxy-acetylene flame is quite sufficient if properly applied.

The cutting and reaming edges of the bit must first be ground clean, as dirt of scale interferes greatly with the application of Stellite.

The blowpipe is adjusted to give a carbonizing flame. The correct flame to use can be arrived at by experiment. Too great an excess of acetylene will deposit a layer of carbon on the molten Stellite, making it difficult to run; too little will cause the Stellite to foam and bubble, due to oxidation. When the flame is correctly adjusted, the Stellite flows freely on the bit. The blowpipe flame is played over the fluke of the bit for a few minutes in order to obtain a low general heat. Starting from the crotch of the bit, the metal is brought to the point of sweating with the blowpipe flame. At the same time the end of the Stellite rod is brought to a molten condition and deposited on the bit, taking care not to puddle the molten Stellite with the bit metal.

Stelliting in this manner is continued along the cutting edge, taking approximately the contour to which the bit wears on being run in the hole. On reaching the reaming edge, stelliting is continued right up the full length, with the object of keeping the bit to gauge. When stelliting the reaming edge, it is necessary to have the edge finished square and flush to the edge of the bit. This is obtained by allowing a small amount of Stellite to flow over the reaming edge, the excess Stellite being finally brought to a plastic or soft condition with the blowpipe flame and struck off flush to the edge of the bit, using a piece of flat steel as a striking-off tool. Fish-tail bits hard-faced with Stellite in this manner can be completed to gauge on the welding-table, and no finished grinding is required.

Tungsten Carbide Inserts. The inserts in this case are approximately $\frac{3}{4}$ in. long by about $\frac{1}{4}$ in. wide and $\frac{1}{4}$ in. thick.

The bit must first be ground clean in the same manner as for stelliting. The procedure is to place the inserts at intervals along the edges of the bit, welding them into place with the blowpipe flame, using a low carbon-steel rod. Having marked the approximate positions on the bit, the insert is tacked to the end of the rod by bringing both to a melting point at the same time, and picking up the insert on the end of the rod. The

position on the bit is then brought to a molten puddle, and the insert is placed in the puddle to a depth of about two-thirds of its thickness. After the inserts have been welded in, the cutting and reaming edges are stellited, covering the inserts. The method of stelliting is the same as for hard-facing with Stellite only. Tungsten carbide inserts are used in this manner, with the object of obtaining a fingered condition on the bit—that is, the inserts, being extremely hard, remain in position, whilst the softer metal in between the inserts wears away, bringing about the fingered effect for which this method is designed. It is claimed that this fingering gives a greater cutting effect to the edge of the bit. It is the author's opinion that if this condition does actually take place, the cutting edge must be considerably weakened and the fingers are liable to break off in the hole. Also it would appear that if this method gives results, the bit should be dressed with finger-shaped points initially. It is reasonable to assume that a considerable amount of wear must take place, and time is lost before this desired condition is arrived at by wear in the drilling operation, when the bit has a straight cutting edge to begin with.

The use of tungsten carbide in powder form is the one method of hard-facing in which it is required to use the carbon arc. An extremely high temperature is required to melt the powder, and it is not suitable for application by the oxy-acetylene process, as the force of the blowpipe flame blows the powder from the job. The bit is ground clean in the usual manner. The powder is placed along the cutting edges of the bit to a depth of about $\frac{1}{4}$ in. and about 1 in. wide. Using a $\frac{3}{8}$ in. carbon electrode on the negative lead of the welding circuit, and with current suitably adjusted, the arc is struck at the edge of the bit. The arc is held close to the powder, which immediately begins to melt into the bit metal. Melting of the powder is continued along the edges until the layer of powder is completely melted into the bit.

This operation must be carried out fairly quickly, as any lingering is liable to generate too much heat, causing the thin edge of the bit to collapse, and leaving hard lumps on the underside, which are practically impossible to remove by grinding.

After the first layer has been melted into the edges of the bit a second layer is placed on and welded in by the same procedure as before. Each succeeding layer increases the hardness of the deposit. Three layers of the powder, it is claimed, give the final desired hardness. When tungsten carbide in powder form was first applied to fish-tail bits in these fields, a considerable amount of trouble was experienced, due to the corners of the bits breaking off in the hole. It is believed that the cause of this was the repeated facing which was necessary on the reaming edge. A fish-tail bit is usually too dull for further running when about 1 in. has been worn off the cutting edge. It will be understood that in this condition there still remains a certain amount of hard-facing material on the reaming edge. In order to allow of the bit being redressed, it is necessary to remove this hard-facing so that, on the bit being dressed again, the reaming edge is subjected to another hard-facing operation. It is believed that repeated facing with the tungsten carbide powder was responsible for the bit becoming carbonized and brittle, causing the breaking of the corners which was experienced. To overcome this disadvantage a method was adopted

whereby the cutting edges only were hard-faced with the tungsten carbide powder and the reaming edges stellited.

The method of hard-facing with composite rod is very much the same as for stelliting. The rod is used in the same manner as Stellite, with the exception that the low carbon steel binding material which holds the small particles of tungsten carbide together is actually welded to the bit steel. The numerous small granules are scattered over the face of the cutting edges and, when the bit is finally completed, the facing has the appearance of a rough emery wheel.

Zublin Regular Bit.

The repair to this type of bit involves a great deal of work in the welding operation. The bit is composed of a heavy shank, with a thrust-pin screwed into the shank at an angle to the shank axis. The thrust-pin acts as a guide for the cutter head, and, being at an inclined angle, causes the cutter head to roll with a " wobbling " motion during the drilling operation.

The cutter head revolves on the thrust-pin by means of hardened steel balls fitted into a ball race on the shank, and the balls also lock the cutter head to the shank proper. The entire bit is liable to severe wear due to the frictional action of the bearing parts when the bit is running, the teeth on the cutter head being the only part of the bit worn through actual contact with the formation of the hole.

To Repair the Shank. The greatest wear takes place on the part of the shank above the ball race, this being the part with which the large cone end of the cutter head comes in contact, when the bit is in operation. Wear at the extreme end takes place to a lesser degree, as this end is protected to some extent by the thrust-pin. To repair the shank, it is first necessary to remove any hard-facing which may be left on the worn parts. This is done by the oxy-acetylene flame. The worn parts are then reinforced or " built up " to size by the metallic arc process with mild steel electrodes. Building up is done to a gauge which allows of about $\frac{3}{16}$ in. being machined off for stelliting. When the hard-facing is being removed, care must be taken to ensure that no small particles of Stellite remain, as these particles, mixing with the built-up weld metal, cause hard spots which cannot be machined. After machining, the shank is hard-faced with Stellite on the part above the ball-race only. The end of the shank next the thrust-pin is machined to finished size, and this part is not hard-faced finally. After stelliting has been completed, the stellited part of the shank is ground to finished size. Grinding is done in a jig, using a portable flexible shaft grinding machine.

The thrust-pin, like the shank, is hard-faced with Stellite. On being returned to the shop in a worn condition, the old Stellite is removed and the thrust-pin is then built up by the metallic arc and machined. After machining, the thrust-pin is stellited and finally ground. All the operations are carried out to gauge sizes to prevent excessive work in machining and grinding. The thrust-pin is finally assembled with the shank.

There are three types of Zublin Bit cutter heads used in this field, and it will be sufficient in describing the methods used in repair to deal with one type only, as the same method applies to all. The cutter head being the actually cutting tool, is naturally subjected to a great deal more wear

than either the shank or the thrust-pin. Apart from the wear which takes place on the cutting teeth, wear of the inside of the head also occurs to some extent, due to the frictional action caused by revolving on the thrust-pin and shank. This condition of wear will be dealt with first. A new cutter head begins to wear on the inner shoulder, which bears on the body of the thrust-pin, on the large and small bores at each end, and on the inside of the bore past the ball race. To build up the worn shoulder inside is a difficult operation by welding. To obviate continual building up and machining of this part of the head, a bearing plate was designed. The shoulder, on becoming worn in the first place, is machined farther back, in order to take the bearing-plate. The bearing-plate is of mild steel cut from a plate to the approximate size with the oxy-acetylene cutter. It is machined to finished size and to the taper of the thrust-pin on which it bears. After being machined the bearing plate is hard-faced with Stellite and ground. It is then tack welded into position inside the cutter head. When the bearing-plate becomes worn, it is only necessary to remove it and replace it with a new one. All other worn parts on the inside of the head are built up to gauges and afterwards machined and ground.

Both the oxy-acetylene and electric metallic arc methods can be used in building up new teeth on worn cutter heads. The practice adopted in these fields at the present time is to build up badly worn heads by the electric arc, and slightly worn heads, where "touching up" only is required, by the oxy-acetylene flame. Using either method the cutter head is finished to size on the welding-table, no grinding or machining being required after welding.

To obtain the required sharp edges on the teeth when building up by the oxy-acetylene flame, the following procedure is adopted. A high carbon steel welder or filler rod is used. The blowpipe is adjusted to a carbonizing flame to prevent "burning out" of the carbon content of the welding rod. The worn base of the tooth and the end of the welding rod are brought to melting point at the same time, and the molten end of the rod is deposited on the molten base metal.

Sufficient metal is added within the control of the welder, and this added weld metal is hammered to shape while hot. Building up by adding more weld metal and hammering to shape is continued until the tooth is finished to size. When the electric arc is used, the operation is a little more difficult, and the procedure adopted in these fields is different from the ordinary routine for building up or reinforcing by metallic arc welding. As the worn base of the tooth is only about 1¼ in. long by 1 in. wide, it will be appreciated that numerous short runs or layers of metal would be required to build up the teeth by the superimposed layer method. Also it would not be possible to obtain sharp edges on the teeth without the further operation of grinding. The method adopted is to use the metallic electrode in much the same manner as the filler rod is used in oxy-acetylene welding. A high carbon-steel electrode is used, and, instead of running the rod in layers, the electrode is puddled over a small area on the base of the tooth, the deposit metal being hammered to shape while hot. This method must not be confused with the carbon arc, in which a separate filler rod is necessary. Building up and hammering are continued, using templates as a guide, until the tooth is completed to size. After building up of the

worn teeth is finished, the teeth are hard-faced with composite rod. The composite rod used in this instance is formed of coarse tungsten carbide particles.

Completed cutter heads are tested on a shank and thrust-pin rigged up on a jig for the purpose and test, and are finally assembled.

Removing Hard-Facing Materials from Fish-tail Bits.

Hard-facing which may remain on worn fish-tail bits is removed by melting and washing off with the oxy-acetylene flame. The procedure is much the same for bits hard-faced with Stellite, Stellite and Inserts, and Composite Rod. The bit is hung in a vertical position with the cutting flukes downward, and a blowpipe of larger size than is used for stelliting is required. The blowpipe is adjusted to a carbonizing flame in the same manner as for the deposit of Stellite. Starting at the top of the hard-facing on the reaming edge, the hard-facing is brought to a molten condition, and in this condition will begin to fall from the face of the bit. The blowpipe flame is then manipulated in such a manner as to propagate the melting of the hard-facing, continuing down the reaming edge and along the cutting edge (if any hard-facing is left) until all hard-facing material is taken off, leaving the bit clean. After a little practice it will be seen that a distinct line of demarcation exists between the Stellite deposit and the parent metal of the bit, and by following this line in the "washing off" process it is possible to remove the hard-facing completely. If the bit has been faced with tungsten carbide inserts covered with a deposit of Stellite, the hard-facing is removed in the same way, the inserts are struck off the face of the bit with a piece of flat steel during the operation of removing the Stellite. The removal of hard-facing composed of composite rod with Stellite binding presents no difficulty, as the small particles of tungsten carbide fall off with the Stellite. It is essential that no hard-facing material whatever is left on the bit, as small pieces of Stellite, etc., if forged into the bit on redressing, will cause cracks in the bit metals.

"Washing off" hard-facing formed by tungsten carbide powder (Britor, etc.) is a more difficult operation. As has already been mentioned, tungsten carbide does not reach a molten condition under the flame of the blowpipe, but slowly oxidizes. Therefore the hard-facing remains in what may be termed a "hard" state, and it is necessary to bring the bit steel behind the hard-facing to such a molten condition as will allow of the tungsten carbide being struck from the face of the bit. There is a greater possibility of "burning" the parent metal when removing hard-facings composed of tungsten carbide powder than with any of the other methods described.

Stellite and tungsten carbide in insert form after reclamation from the worn bit can be used again. The Stellite is melted in a crucible and cast into rod form. Inserts are used in the same condition as they are taken from the worn bit. Hard-facing formed from the deposit of tungsten carbide powder when melted from the bit is practically slag, and is of no further use.

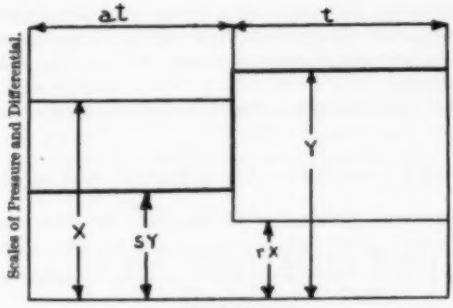
INTEGRATION ERRORS IN THE MEASUREMENT OF GAS FLOWS THROUGH AN ORIFICE.

ERRORS INCURRED BY EMPLOYING A SQUARE-ROOT PLANIMETER, IN THE COMPUTATION OF FLOW CHARTS FOR COMPRESSIBLE FLUIDS.*

By H. Gilmour, B.Sc.

In a previous paper on the subject of "Integration and Pulsation Errors in Orifice Measurement of Gas Flows" (*J.I.P.T.*, 1933, **19**, 25–68) no mention was made of errors incurred when employing a square-root planimeter. As the square-root planimeter undoubtedly offers a very reliable and rapid method for chart integration, provided that certain precautions are taken, and is eminently suited to the requirements of oil-field practice, the subject of liability to error, when integrating with this instrument, warrants close investigation.

The necessity for careful application and manipulation of this useful instrument can be very clearly demonstrated by the following simple mathematical investigation. The simplest form of investigation, offering easy mathematical solution, is that of the hypothetical case, in which the variables, the static pressure and the differential across the orifice are "square-form" curves, changing values simultaneously, as shown in the following flow chart :—



Flow Chart.

The above flow chart represents a record taken during a period of time $(at + t)$, of the absolute static pressure within the flow pipe, upstream of the measurement orifice, and of the differential pressure across the orifice. During the first period, at, the static pressure and differential were uniform at the values X and sY, respectively, and during the succeeding period, t, the corresponding values were rX and Y.

* Paper read before the Burma Branch of the Institution of Petroleum Technologists.

Consequently

$$a = \frac{\text{1st period of time}}{\text{2nd period of time}},$$

$$r = \frac{\text{Absolute static press. during period, } t}{\text{Absolute static press. during period, } at},$$

and

$$s = \frac{\text{Differential press. during time, } at}{\text{Differential press. during time, } t}.$$

The general equation of flow of a compressible fluid through an orifice under specified conditions is given by the equation :—

$$Q = K\sqrt{P \times H}$$

where Q = quantity of gas which has passed through the orifice in a unit of time,

K = a flow constant, depending on the orifice and pipe diameters, positions of meter connections, specific gravity and temperature of gas (all conditions assumed constant during the unit of time),

K, therefore, is the total quantity of gas passing through the orifice in a unit of time, when the differential and static pressures are both unity,

P = the absolute static pressure within the flow pipe on the upstream side of the orifice, and

H = the differential pressure across the orifice, usually expressed in head of water.

As the flow rate is proportional to the function, $\sqrt{PH}$, the quantity which passes through the orifice in a given time can only be determined visually by integration of the flow chart for each successive period during which both P and H are reasonably constant (see note which appeared in the previous paper).

Consequently, the true total flow through the orifice in time $(at + t)$ is :—

$$Q = K\ (\text{at } \sqrt{sX}Y + t\sqrt{rX}Y) = Kt\sqrt{XY}(a\sqrt{s} + \sqrt{r}) \text{ cubic feet} \quad . \quad (1)$$

Using a square-root planimeter to integrate the diagram, we get :—

$$Q_1 = K(at + t)\left\{\frac{at\sqrt{X} + t\sqrt{rX}}{(at + t)}\right\}\left\{\frac{at\sqrt{sY} + t\sqrt{Y}}{(at + t)}\right\} \text{ cubic feet at N.T.P.}$$

$$= Kt\sqrt{XY}\,\frac{(a + \sqrt{r})(a\sqrt{s} + 1)}{(a + 1)} \text{ cubic feet at N.T.P.} \quad . \quad . \quad . \quad (2)$$

$$\therefore \text{ Error ratio} = \frac{Q_1}{Q} = \frac{(a + \sqrt{r})(a\sqrt{s} + 1)}{(a + 1)(a\sqrt{s} + \sqrt{r})} \quad . \quad . \quad . \quad (3)$$

$\therefore$ % error in measurement by planimeter

$$= \left\{\frac{(a + \sqrt{r})(a\sqrt{s} + 1)}{(a + 1)(a\sqrt{s} + \sqrt{r})} - 1\right\} \times 100\% \quad . \quad . \quad . \quad (4)$$

To determine error when either pressure or differential are constant, equate $r = 1$.

The error ratio $= \dfrac{(a+1)(a\sqrt{s}+1)}{(a+1)(a\sqrt{s}+1)} = 1$

also, equating $s = 1$ ratio $= \dfrac{(a+\sqrt{r})(a+1)}{(a+1)(a+\sqrt{r})} = 1$

i.e. there is *no error* in integration, using a square-root planimeter, if *either* the pressure *or* differential remain constant throughout.

To determine the maximum error ratio for any values of s *and* r.

The value of factor a, for which the error ratio is a maximum for any particular values of s and r, is given by equating :—

$$\frac{d}{da}\frac{(a+\sqrt{r})(a\sqrt{s}+1)}{(a+1)(a\sqrt{s}+\sqrt{r})} = 0$$

Differentiating we get

$$a = \sqrt[4]{\frac{r}{s}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the maximum error ratio for any particular values of s and r given by :—

$$\frac{(\sqrt[4]{r}+\sqrt[4]{s}\sqrt{r})(\sqrt[4]{r}\sqrt{s}+\sqrt[4]{s})}{(\sqrt[4]{r}+\sqrt[4]{s})(\sqrt[4]{r}\sqrt{s}+\sqrt{r}\sqrt[4]{s})} = \text{maximum error ratio} \quad . \quad (6)$$

(See Graph No. 3.)

In order to limit the field of investigation, we may assume that, in actual practice, the variation in the static pressure rarely exceeds the range, which would result in the factor s having a range in values, say, between 8·0 and 0·2. The factors a and r can have any positive values, but, whereas it is evident that the planimeter error would be very great for very high and low values of r, it is equally obvious that the error is very small for extremely large and small values of factor a.

TABLE I.

Percentage Integration Error by Square-root Planimeter, Factor a = 1·000.

Values of a.	Values of factor, r.											
	20·0.	10·0.	5·0.	2·0.	1·0.	0·8.	0·6.	0·5.	0·4.	0·2.	0·1.	0·0.
	%	%	%	%	%	%	%	%	%	%	%	%
10	49·1	37·0	24·7	9·7	0	−2·7	−6·2	−8·2	−10·5	−19·5	−21·13	−34·2
8	43·5	33·0	22·3	9·1	0	−2·5	−5·7	−7·6	− 9·7	−15·4	−19·9	−32·3
5	32·0	24·7	17·0	7·0	0	−2·1	−4·6	−6·1	− 7·9	−12·7	−16·5	−27·6
4	26·9	20·9	14·4	5·3	0	−1·8	−4·1	−5·4	− 7·0	−11·3	−14·8	−25·0
2	12·2	9·7	7·0	3·0	0	−0·9	−2·2	−2·9	− 3·7	− 6·1	− 9·2	−14·3
1·0	0	0	0	0	0	0	0	0	0	0	0	0
0·8	− 3·4	− 2·8	− 2·1	−0·9	0	0·3	0·7	0·9	1·4	2·2	3·0	5·9
0·6	− 7·5	− 6·2	− 4·6	−2·1	0	0·7	1·0	2·2	3·0	5·1	6·8	14·6
0·4	−12·5	−10·5	− 7·9	−3·8	0	1·4	3·0	4·0	5·4	9·4	13·2	29·1
0·2	−19·5	−16·5	−12·7	−6·1	0	2·2	5·1	7·0	9·4	17·0	24·7	61·8

TABLE II.

For $a = 0{\cdot}5$.

Percentage Errors for Values of s *and* r *Less Than Unity.*

Values of s.	Values of r.						
	0·8.	0·6.	0·5.	0·4.	0·2.	0·1.	0·0.
0·8	0·25%	0·7%	0·9%	1·4%	2·2%	3·2%	7·8%
0·6	0·6	1·4	2·0	2·7	4·9	7·3	19·4
0·5	0·8	2·0	2·8	3·6	6·8	10·4	28·0
0·4	1·05	2·5	3·5	4·7	8·8	13·2	38·8
0·2	1·7	4·15	5·8	7·9	15·2	23·4	82·4

TABLE III.

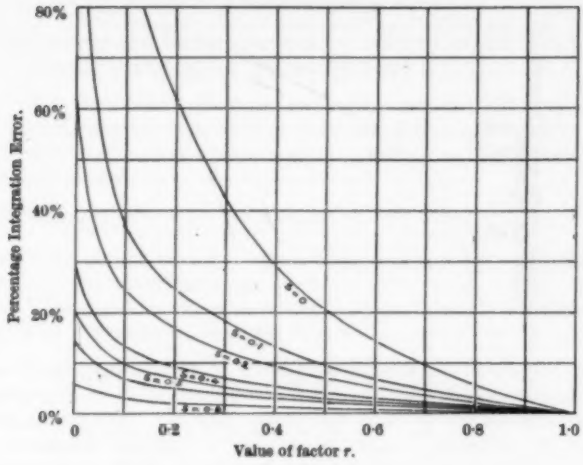
For $a = 2{\cdot}000$.

Percentage Errors for Values of s *and* r *Less Than Unity.*

Values of s.	Values of r.						
	0·8.	0·6.	0·5.	0·4.	0·2.	0·1.	0·0.
0·8	0·25%	0·7%	0·8%	1·1%	1·7%	2·3%	4·0%
0·6	0·7	1·4	2·0	2·5	4·2	5·5	9·7
0·5	0·9	2·0	2·8	3·5	5·8	7·6	13·8
0·4	1·4	2·7	3·6	4·7	7·9	10·6	19·4
0·2	2·2	4·9	6·8	8·9	15·2	20·8	41·2

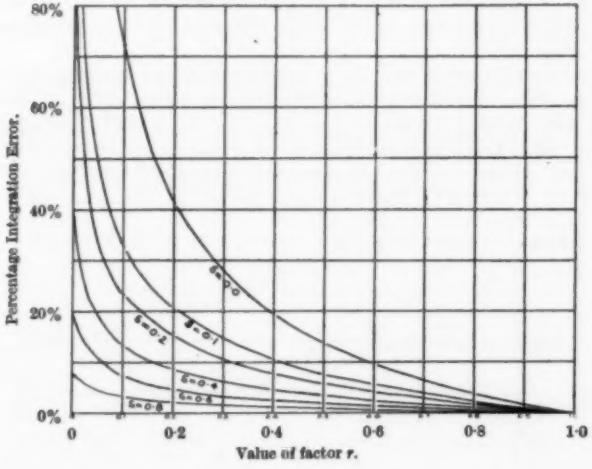
The Values of Factor a *for Maximum Error for Differential Values of* r *and* s. *Table of Values of* a *for Maximum Error.*

Values of s.	Values of r.						
	0·8.	0·6.	0·5.	0·4.	0·2.	0·1.	0.
8·0	0·56%	0·52%	0·50%	0·47%	0·40%	0·33%	0%
6·0	0·60	0·56	0·54	0·50	0·43	0·36	0
4·0	0·67	0·62	0·59	0·56	0·47	0·40	0
2·0	0·80	0·74	0·71	0·67	0·56	0·47	0
0·8	1·00	0·93	0·89	0·84	0·71	0·59	0
0·6	1·08	1·00	0·96	0·90	0·76	0·64	0
0·5	1·13	1·05	1·00	0·95	0·80	0·67	0
0·4	1·19	1·11	1·05	1·00	0·84	0·71	0
0·2	1·42	1·32	1·26	1·19	1·00	0·84	0
0·1	1·68	1·57	1·50	1·42	1·19	1·00	0



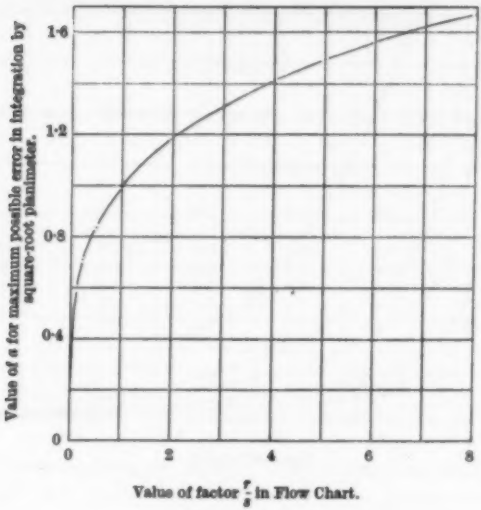
GRAPH No. 1.

GRAPH OF PERCENTAGE ERROR USING A SQUARE-ROOT PLANIMETER WHEN FACTOR a IN FLOW CHART IS 1·0 FOR VALUES OF FACTORS LYING BETWEEN 0·0 AND 1·0.



GRAPH No. 2.

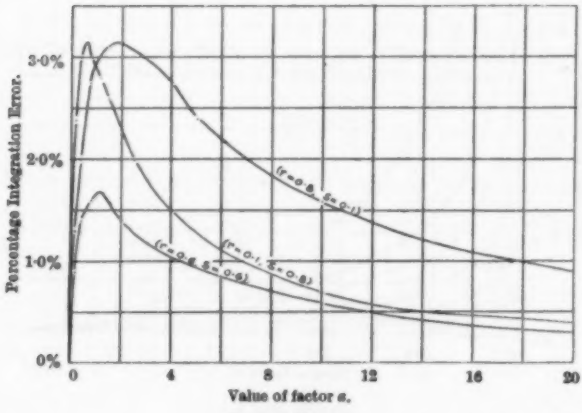
GRAPH SHOWING PERCENTAGE INTEGRATION ERROR, WHEN EMPLOYING A SQUARE-ROOT PLANIMETER, VALUE OF TIME FACTOR a BEING 0·5 (SEE FLOW CHART) FOR VALUES OF FACTOR r LYING BETWEEN 0·0 AND 0·1.



GRAPH No. 3.

GRAPH SHOWING VALUES OF a IN FLOW CHART FOR MAXIMUM INTEGRATION ERROR, USING A SQUARE-ROOT PLANIMETER, ON A BASE OF RATIO $\frac{r}{s}$. FOR MAXIMUM ERROR,

$$a^2 = \sqrt{\frac{r}{s}}; \quad a = \sqrt[4]{\frac{r}{s}}$$



GRAPH No. 4.

GRAPH SHOWING EFFECT OF CHANGE IN THE VALUE OF FACTOR a UPON THE PERCENTAGE INTEGRATION ERROR IN TWO CASES WHERE THE FACTORS r OR s VARY GREATLY AND IN ONE CASE WHERE BOTH VARY MORE MODERATELY.

Conclusions.

From the graphs and tables prepared for different values of a, it is clear that the square-root planimeter integration error is :—

(1) A positive error when the static pressure and differential change antipathetically (*i.e.* the total is in excess of the true value).

(2) A negative error when the static pressure and differential change sympathetically.

(3) Greatest, when a approximates to the value $\sqrt[4]{\frac{r}{s}}$.

(4) Very big for extreme values of r; particularly when the values of a lie at the same extreme.

(5) Very small for extreme values of a; particularly when the values of r lie at the opposite extreme.

No useful purpose would be served by examining the errors resulting from integration of flow, during which the changes in the variable do not occur simultaneously. In any particular case in actual practice it is easy to recognize whether or not the error is appreciable by reference to the conclusions obtained from the hypothetical case already discussed. If the error be appreciable, it may be practicable to planimeter the chart for successive periods, during which the differential and pressure variations are insufficient to incur any appreciable error. This involves integration in sections. In certain cases where this alternative method is impracticable, due to relatively high frequency of the variations, which variations are cyclically reproduced, it is possible to apply a correction factor, provided that the range of either of the variables is comparatively small.

Wherever possible, the best solution of all is to design the measurement installation, so that either the differential or pressure is maintained at a constant value. This is, in fact, the only solution for cases for which the above methods of integration are impracticable. The most economic method of obtaining the desired result was fully dealt with in "Integration Errors in Measurement of Variable and Pulsating Flows."

DETERMINATION OF THE CLOUD POINT OF DARK OIL.*

By W. R. Van Wijk.†

Introduction.

At the World Petroleum Congress in 1933 Verver (*Proc. World Petr. Congr.*, 1933, **2**, 417–418) described a method for the determination of the cloud point of dark oil. This was based on refining the oil to a light enough shade to permit of visual observation of the appearance of turbidity in the oil.

The method is suitable for many practical purposes, and generally speaking it is possible in this way to observe the separation of paraffin wax in diesel fuel, which separation might cause difficulties by precluding filtration. There are oils which are so dark that no, or only very radical, refining is capable of making them sufficiently transparent, and for practical reasons the cloud point even of these oils is often a matter of interest. Furthermore, a need was felt from the theoretical standpoint for a method of determining the cloud point of dark oil.

During an investigation into the influence of pour-point reducers on the pour point, the question arose as to whether the cloud point is at all influenced by neutral pour-point reducers. If so, the determination of the cloud point after refining would, of course, become impossible, because natural pour-point reducers may be removed during refining.

This paper is not concerned with such questions, its sole aim being to describe a method by which the cloud point of the original oil can be determined without any preliminary treatment beyond drying.

Principle of the Method.

In principle the method depends on the measurement of the transmittancy of the oil to infra-red radiation at various temperatures, a dark oil being far more transparent to radiation of 1 to 3 microns wave-length than to visible light. If there is any separation in the oil, the medium diminishes in transmittancy owing to its optical inhomogeneity, allowing of conclusions being reached from the course of the transmittancy–temperature curve as to the separated matter in the oil. In this way the separation may be detected not only of, say, paraffin wax crystals, but also of traces of substances left over from refining, of asphaltenes and of other matter.

Before proceeding to describe the equipment and the determinations, we should like to examine how the transmittancy of the oil may change with the temperature.

* Paper received August 5th, 1936.
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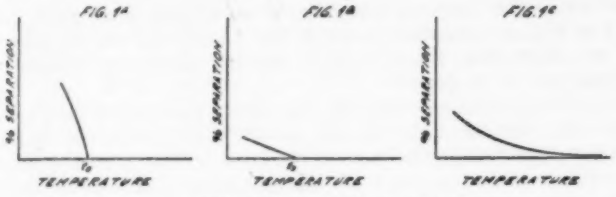
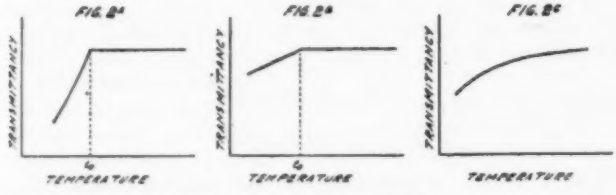
In the first place, it may be that the oil is perfectly homogeneous at high temperature. On cooling, the oil then remains homogeneous for some time until a certain temperature, t_0, is reached, when separation occurs. Such an oil has a true cloud point, viz., t_0. Had the oil been transparent, so that visual detection of the cloud point would have been possible, t_0 would have been found to be the cloud point, in the event that the separated quantity of material would have increased rapidly at temperatures below t_0. Since in the visual method the cloud point as recorded is a temperature



SEPARATION CONTENT OF OILS.

at which separation is present in a sufficient degree to be properly perceived, a lower temperature than t_0 would have been found if the quantity of separated matter had increased only very slowly at temperatures below t_0. In the latter case the cloud point would perhaps be designated as "vague," or "not clearly defined."

It is a different matter when separated substances occur in the oil even at high temperature, increasing in quantity as the temperature falls. Such an oil has no cloud point, as no temperature can be indicated at which cloudiness suddenly appears. Had this oil been transparent, the operator would probably have designated the cloud point as badly defined.



TRANSMITTANCY OF OILS.

In the accompanying graph (Fig. 1) the quantity of separated substance is plotted against the temperature for the three cases under discussion. Corresponding with these curves—quantity of separated matter plotted against temperature—there are transmission curves of the types shown in Fig. 2. Figs. 2*a* and 2*b* represent the case of the oils given in 1*a* and 1*b*, *i.e.*, in which the oil possesses a true cloud point.

Fig. 2*c* represents the case of an oil without cloud point. Thus in all cases at high temperature the oil is invariably more transparent to infra-red rays than at low temperature, so that, when the oil is cooled down, the transmittancy decreases, which may take place either gradually (2*c*), or

suddenly (2*a* and 2*b*). These different cases have been actually observed in practice.

Moreover, transitional cases were found in which the oil appeared to be free from inhomogeneities at high temperatures, whereas at low temperature they did occur, the transmittancy curve showing, however, no break, but a continuous transition. Thus by drawing a smooth curve through the points of determination of the transmittancy for infra-red radiation, one will find the cloud point clearly defined in the cases represented in 2*a* and 2*b* and no cloud point for the case represented in 2*c*. In the transitional case, if the range of transition is small, the cloud point could be defined as that temperature at which the tangent line to the part of the curve in which the transmittancy rapidly diminishes intersects the horizontal part of the curve.

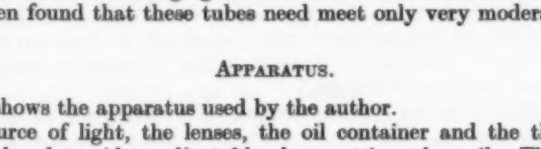
As to the applicability of the test, the author was able to measure all the oils, even the darkest, which he had to deal with. Since the transmitted intensity depends on the thickness of the layer as well as on the absorption characteristics of the respective oil, different layer thicknesses of the oil will have to be used, according to the depth of colour of the oil, to obtain approximately the same order of transmitted intensity. To this end the author used tubes ranging from about 5 cm. to 0·5 cm. in diameter. It has been found that these tubes need meet only very moderate optical demands.

Apparatus.

Fig. 3 shows the apparatus used by the author.

The source of light, the lenses, the oil container and the thermo-pile were all placed on riders adjustable along a triangular rail. The rail was

FIG. 3



SKETCH OF ASSEMBLAGE.

mounted on a board. A galvanometer was coupled to the thermo-pile by a flexible cord and was placed apart. The source of light was a small electric lamp 6 V. 35 W., as used in motor-cars, with a straight short spiral (about 1·2 mm. in dia. and 2·5 mm. long). An image of this spiral was thrown by a single lens of 12 D. in the centre of the oil container. This container consisted usually of an A.S.T.M. pour-point glass submerged in a cooling liquid in an unsilvered Dewar vessel mounted on a rider. The beam of rays passing through the Dewar vessel was concentrated on the thermo-pile by a second single lens of 20 D. The oil was cooled by dropping pieces of solid carbon dioxide into the cooling liquid, so that the bubbles rising caused the cooling fluid to be stirred, using carbon tetrachloride for temperatures down to −20° C. and acetone for lower temperatures. By means of a small immersion heater the bath could be heated

to about 60° C. Both in the cooling liquid and in the oil a thermometer was hung. The cooling was regulated so that the difference in temperature between the bath and the oil was at most 3° C., resulting in a rate of cooling of the oil of about 0·3° C. per minute. The number of samples that can be tested at a time depends on the number of measuring points on the transmittancy curve and the skill of the operator. It would be about six, if a determination were made every other degree Centigrade.

The reproducibility of the adjustment of the Dewar vessel proved to be so good that this could safely be taken from the apparatus and replaced by another and then put back into the apparatus again for the next measurement. The position of the Dewar vessel is fixed by a stop screwed to the board and fitting the rail, against which stop the rider with the Dewar vessel is slid. In this manner the vessel could rapidly be returned to its original position, and so exactly, too, that the deflection of the galvanometer obtained after replacement of the Dewar vessel deviated less than about 0·2 per cent. from the deflection obtained before removing the Dewar vessel.

A very delicate part of the apparatus proved to be the source of light. To avoid undesirable fluctuations in the intensity of the radiation it proved to be necessary to solder the supply cords to the lamp and to connect the lamp to a separate storage battery. By means of a fixed and a variable resistance interconnected in parallel and connected in series with the lamp, the intensity of the radiation was regulated to obtain a satisfactory deflection of the galvanometer.

The variable resistance served also to compensate for the slow decrease in voltage of the storage battery. The fixed resistance was interchangeable and allowed of a rough adjustment of the intensity.

As concerns the thermo-pile, any sensitive type of thermo-pile can be used; the thermo-pile used by the author gave about 1 μV., when exposed to a radiation of 1 W. per 4 π sq. m. It was used in connection with a simple type of galvanometer (sensitivity about 1μ A. for 1 cm. deflection on 100-cm. scale distance, resistance 60Ω). The time in which the system (pile plus galvanometer) gave a registration up to 95 per cent. of the final deflection was less than about 0·8 second.

The pour-point glass in which the oil was put was fitted in a simple holder to the Dewar vessel. A diagram of this holder is given in Fig. 4.

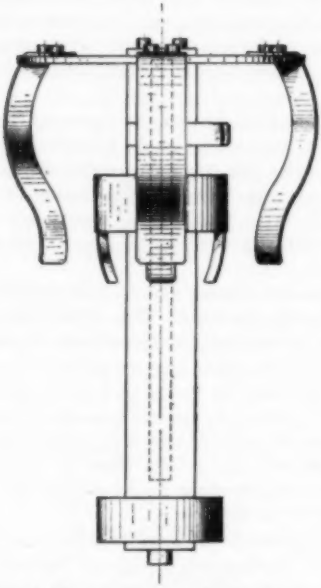
For very dark oil a pour-point glass was used, part of which was restricted so that the thickness of the layer through which the rays are to pass was about 4 mm.

The distances between the lamp and the first lens and between the first and second lens were 17 and 30 cm. respectively. The thermo-pile was placed 7·5 cm. beyond the second lens. The internal diameter of the Dewar vessel used was 6 cm.

As the Dewar vessel containing cooling liquid and oil acted as a cylindrical lens, rays emanating from a point of the glow spiral were not united again in one point, so that a true image of the glow spiral on the thermo-pile could not be obtained, but the rays drew together to two focal lines, one of which ran parallel to the axis of the Dewar vessel (vertical focal line), and the other being at right angles to it (horizontal focal line). When using carbon tetrachloride with a refractive index of 1·46 as cooling liquid, the

distance between these focal lines was about 1 cm. The thermo-pile was placed in the centre between the focal lines. The intensity of the light in this place was practically homogeneous over a small area, so that on the axis of the Dewar vessel being turned over, only a comparatively slight fluctuation in intensity would result at the soldering places of the thermo-pile. The influence of a movement forwards or backwards of the Dewar vessel was also found to be less than would be the case if the thermo-pile was placed in one of the focal lines. The reproducibility of the adjustment of the arrangement was further experimentally investigated.

FIG. 4.



Holder for pour point glass.

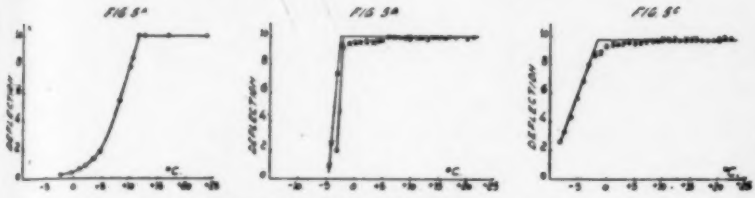
By turning over the axis of the Dewar vessel through a given angle, variations up to 3 per cent. were observed in the deflection of the galvanometer, if the thermo-pile were placed *between* the two focal lines, while when repeating the measurements after placing the thermo-pile in one of the focal lines, somewhat greater variations were found. The angles of deviation of the axis of the Dewar vessel applied in these experiments were, however, much greater than those occurring in actual practice.

From a series of measurements after each of which the Dewar vessel was taken away and adjusted again correctly, it appeared that under otherwise identical conditions the deflections of the galvanometer deviated less than 0·2 per cent. so that there are no objections to cooling several

samples in different Dewar vessels at a time and measuring them one after another in the same apparatus.

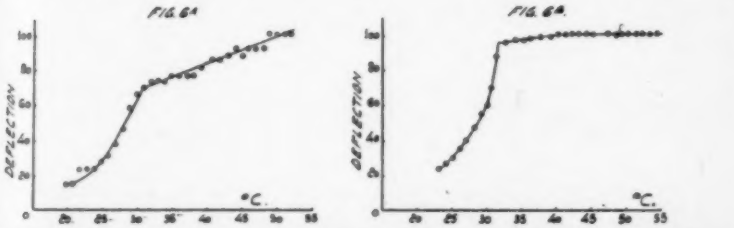
Results.

As illustrations of the curves that may be obtained with the aid of the apparatus we give in Figs. 5*a*, *b* and *c* three examples of measurements applied to lubricating oil (machine oil).



Transmittancy of machine oils.

The oil in Fig. 5*a* has a well-defined cloud point (at 11·5° C.); the oils in 5*b* and 5*c* have a small transition region. The latter measurements were made in duplicate, the crosses indicate the points found in the first measurement, the circles those of the second observation. It will be observed that the measurements agree satisfactorily. With oils that were of such a light colour that they could also be measured visually, the cloud points measured with the apparatus were invariably found to tally well with those observed visually (maximum deviation 0·5° C.) in cases where the oil had a sharply defined cloud point. The oils in Fig. 5*a*, *b* and *c* were all



Transmittancy of a very dark fuel before and after deasphaltizing with pentane.

sufficiently transparent to allow of their being measured in a layer 3·2 cm. thick, *i.e.*, in a normal pour-point glass.

As an example of a very dark oil, we give in Fig. 6*a* the curve of transmittancy of a fuel oil containing 2·0 per cent. of asphaltenes and which had to be measured in a layer 0·4 cm. thick. This fuel, also at high temperatures, contains a separation, viz., asphaltenes. During cooling the separation increases: at 31° C. there is a break in the curve of transmittancy owing to the separation of paraffin wax. In Fig. 6*b* the curve of transmittancy of the same oil is given, after the asphaltenes had been

precipitated by pentane; the removal of the asphaltenes has evidently had no effect upon the cloud point. These examples will serve to illustrate the applicability of the method.

The author considers the advantage of this method to consist not only in the possibility of indicating separations in dark oils, but also in that of following objectively, and also more or less quantitatively, the entire process of separation as a function of the temperature.

The method has also been successfully applied in other cases for measuring turbidities in oil, for instance for the determination of the demixing curves of unrefined lubricating oil and solvents and for the determination of the aniline point of dark oil.

The author wishes to express his gratitude to the Managers of the Bataafsche Petroleum Maatschappij for their permission to publish this investigation, and to Mr. B. H. Moerbeek of the Amsterdam Laboratory for much valuable information and a number of suggestions.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

EIGHTEENTH ANNUAL DINNER

THE Eighteenth Annual Dinner of the Institution of Petroleum Technologists was held at the Connaught Rooms, London, on Friday, October 9th, 1936, the President, Sir John Cadman, G.C.M.G., occupying the Chair.

"HIS MAJESTY THE KING"

The Toast "His Majesty the King" was proposed by the President and loyally accorded.

"THE INSTITUTION OF PETROLEUM TECHNOLOGISTS"

Brig.-Gen. Sir SAMUEL H. WILSON, G.C.M.G., K.C.B., K.B.E.: You have done me a very great honour to-night in entrusting me with the important duty of proposing the health of your Institution. At the same time, I rise to do so with no little trepidation, because, in spite of your Chairman having lent me a volume of over 200 pages describing what wonderful work your Institution has done in the last twenty-one years, I cannot help feeling that even now I do not grasp everything that I have read. I hope you will sympathize with my point of view when I remind you that there must be a lot of people in this gathering who have been almost born and bred in oil, while I have been a soldier most of my life. Until about fifteen years ago, when I became Governor of Trinidad, I had practically no experience at all and knew very little about this indispensable commodity, oil. Indeed, although I had often heard the expression "the winning of oil," I had no idea how the commodity was procured from the earth until within about ten days of my assuming the Governorship of Trinidad.

On the occasion in question I was very kindly invited to pay a visit to one of the oil-fields, in Trinidad, and to bring with me a party of guests who were staying at Government House, which included the present Secretary of State for the Colonies, Lord Salisbury, and Lord Halifax. On reaching the well on the oil-field that had recently been brought in, we were warned by our hosts not to go beyond a certain distance; but the next thing I saw was Lord Salisbury climbing up a mound to get a better view, and, in true schoolboy style, I followed him, not wishing to be outdone. The next I knew was that my new white hat and nice new grey suit, which I put on in order to go to my first garden-party in Trinidad on our way home to Port of Spain, was more like one of those spotted dogs which I think used to be called plum-pudding dogs, than the clothes of the King's Representative.

I naturally heard a good deal about oil during the four years that I was Governor of Trinidad, and then at Jamaica, and subsequently during

the eight years that I was head of the Colonial Office; but it was not until about eighteen months ago that I became, if I may say so, one of the family, when I was asked to join the Board of the Apex (Trinidad) Oilfields, Limited.

In proposing the toast of your Institution I am to be supported by Sir Claud Hollis, who has just come back after having been Governor of Trinidad for six years. I have no doubt he will tell you the very latest news of the Trinidad oil-fields. I thank you for having invited me to-night. (Applause.)

Sir ALFRED CLAUD HOLLIS, G.C.M.G., C.B.E.: I rise in response to a request from your President that I should say a few words in support of Sir Samuel Wilson, and I hope I shall not be guilty of rushing in where he, as an angel, has feared to tread. (Laughter.)

The application of science has had a profound influence in moulding and shaping the modern world. You may remember that the late Lord Moulton once said that the progress of human power over Nature was achieved by workers of three distinct classes: the scientific investigator, the inventor and the technologist. The contrast between the scientific discoverer and the technical giants who follow him can, I think, be well illustrated by two quotations from Milton's "Paradise Lost." Before I give you these quotations I should like to mention that I asked my friend on the right whether he thought that quotations from Milton's "Paradise Lost" would be appropriate, and he told me that, seeing that no body of people is more nearly allied to the Devil than a body of scientists, he felt sure they would be appreciated. (Laughter.)

Well, gentlemen, the quotations refer to the time when Satan toiled through the vast void to reach our Earth, and his progress is thus described:—

> "So he with difficulty and labour hard
> Moved on—with difficulty and labour he."

But once he had passed through the wide expanse, his companions, Sin and Death:—

> "Following his track—such was the will of Heaven—
> Paved after him a broad and beaten way
> Over the dark abyss."

The one as a pioneer finds his way with doubt and difficulty through the unknown until he has unravelled the mystery and revealed the truth that he is seeking, and that is his triumph; but the triumph of the others is the broad and beaten way which they make after the truth has been arrived at, so that all can avail themselves of its results.

The whole record of industrialism contains nothing to approach the phenomenal rise of the oil industry to its present dominant position. It has been said that we live in an oil age. Notwithstanding this, but few people are aware of the large number of products that owe their origin to petroleum. I am reliably informed that they can be counted in hundreds, if not in thousands; and they range from coke to cosmetics, from lubricants to luminants, from soaps to solvents, from insecticides to floor polishes, from lipsticks to explosives, from asphalt to chewing-gum, and from cleaning spirit to a purge. (Laughter.)

As Sir Samuel has just told you, I have recently returned from Trinidad, where a branch of the Institution of Petroleum Technologists was formed in 1931. The importance of the industry to that Colony may be gathered from the fact that the export of oil and its products is annually valued at about £3,000,000 sterling, or 60 per cent. of the Colony's total exports.

I now ask you to drink to the Institution of Petroleum Technologists, which, although of recent formation—I believe it was founded in 1913—has already become world-wide in its activities, cosmopolitan in its membership and comprehensive of the whole of the science and technology of petroleum. (Applause.)

The toast "The Institution of Petroleum Technologists," coupled with the name of the President, Sir John Cadman, was enthusiastically received.

THE PRESIDENT, Sir JOHN CADMAN, G.C.M.G.: We are really privileged in having at the same time two great Colonial administrators at our Banquet. I think this is the first occasion on which we have had the benefit of having the health of the Institution proposed by such distinguished friends. ("Hear, hear.") The fact that both these great administrators have had their birth and upbringing in oil in that delightful Colony of Trinidad makes it more pleasing to us, because many of our Members have served their time in that Colony.

I feel tempted to say something of that wonderful island of which these two distinguished friends have spoken to-night, and to give a little history of the oil of Trinidad; but that would occupy too long. I will not say that I had my birth in oil in Trinidad, but I certainly was there at the birth of the oil industry. I was sent out to administer legislation in connection with one of the natural residues of oil—asphalt—and it was there that I began to study the possibilities of oil in that Colony. At that time there was one area which was being attacked by a Canadian Company, and I am delighted to hear to-night from one of my friends that this area is now being drilled again, and is likely to be successful.

You, Sir Claud, have referred to the inception of the Institution as taking place in 1913–1914. It started at a time when some of us felt—and Sir Boverton Redwood particularly—that there was a gap in the societies which embraced the different branches of technology. We fill the gap by providing common ground for the engineers, the chemists, and the geologists who took part in the making of what we now know as the Institution of Petroleum Technologists.

This Institution is composed of members of a great industry. They are all experts who form part of a great administrative working element which really makes the oil industry alive; and they are actually employed in the industry—not merely consulted from time to time.

The Institution has had another successful year. It came of age, as you are aware, in 1935; but the attainment of maturity has not prevented further growth. In fact, a satisfactory increase of membership—from 1300 to 1400—has been obtained.

In saying that the increase has been satisfactory, however, I must make certain reservations. It has occurred to many of us during recent years that the structure of the Institution, excellent as it was in the early years, has, perhaps, become too restricted for present conditions. At the time

of the inception of the Institution the term "Petroleum Technologist" was given what we then rightly regarded as a liberal interpretation. Times, however, have changed. The industry has expanded and has developed many ramifications. There is a widespread feeling that the title of petroleum technologist ought not to be confined solely to geologists, engineers and chemists. A man who markets oil should be as skilled in his own line as any other technologist. I trust that neither oil accountants nor chemists would be affronted if I suggested that each class carries out technical activities, and that neither could do the work of the other.

The Council of the Institution is giving thought to the desirability of widening the scope of the Institution. A number of problems will have to be solved. All present members, however, may be assured that nothing will be proposed which would reduce the utility of the Institution or lessen the high prestige it now enjoys. In fact, the aim will be towards rendering membership of the Institution an even higher credential than it now is.

I think you will agree that a widening of scope would be appropriate to the trend of petroleum activities at the present time. In Great Britain, for instance, oil and oil affairs are much to the forefront. For the first time since the efforts of Pearson and Company in the years 1918–1922, oil prospecting operations are being undertaken here. Licences covering nearly 8000 square miles have been issued, and I am sure that the holders of those licences are determined to establish a British oil-producing industry if Nature has provided the essential oil itself.

If an oil-producing industry is established here, we shall have certain advantages over our confrères in the United States. Notable among those advantages is the fact that there will be none of the exploitation in small plots which has been so detrimental an influence in that country. National reserves of oil, if they exist in Great Britain, will be developed in a sane and orderly manner. For that prospect, the nation—and ourselves in our concerns with oil—should be thankful to the wisdom of our legislature.

In the course of the work which is being done in the South of England, which is being attacked at the present moment, seepages have been discovered. I have, in fact, on one occasion sat in one, and spoiled a thoroughly good pair of pants in doing so. (Laughter.) In order to make it quite clear that these seepages do occur, I am going to pass round the first sample of natural oil which my colleague Mr. Jameson produced for me the other day when he and Dr. Lees examined some outcrops. They took about a bucketful of oil, with some effort, produced a bottle and brought it in to show me. It is the genuine article. I am going to pass it round, and you shall see a sample of real live oil which has been taken from a seepage in this country.

May I say I am delighted to hear that the Institution is going to pay a visit to the Portsdown Well to-morrow, and I want to extend a very hearty welcome to Members to see that plant in operation. You will see one of the finest equipments that can be produced. It is not travelling at a pace which normal oil-field practice demands; the care and caution that are being taken to examine almost every bit of the section by coring has made it much slower than it otherwise would be. Naturally we have

[*Fradelle and Young.*

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

EIGHTEENTH ANNUAL DINNER, OCTOBER 9TH, 1936.

Standing (left to right): H. J. Pooley, Dr. J. J. Fox, O.B.E., D. J. Lochtie, Lt.-Col. S. J. M. Auld, O.B.E., M.C., Sir Alfred Claud Hollis, G.C.M.G., C.B.E., Brig.-Gen. Sir Samuel H. Wilson, G.C.M.G., K.C.B., K.B.E., Sir John Cadman, G.C.M.G. (President), F. C. Starling, J. B. Aug. Kessler, A. de Boulard, Major F. C. Cook, D.S.O., M.C., E. S. Shrapnell-Smith, C.B.E., H. T. Young, Prof. O. T. Jones, P. C. Kidner.

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had some little disappointments in regard to it. Whereas surface evidence has suggested that oil would be found under the tectonic conditions which exist there, we have been disappointed in the one case to find the rocks were as solid as a piece of indiarubber, and there is no chance of any oil being conserved in that particular part. But that does not alter the evidence; if we can find the structural conditions with the necessary porosity, and if it is possible for the oil to be conserved—floated up on the top of water—in these regions, we are going to find some oil, and we are not going to give it up until we have settled once and for all whether oil is to be found in this country. (Applause.)

I have said we should be thankful for the wisdom of our legislature, and I am glad to have the opportunity to-night of paying a tribute to our friend Mr. Starling, who took such a great part in that matter. (Applause.)

The possibility of the establishment of an oil-producing industry leads one to hope that public knowledge of oil and oil affairs will gradually be raised above its present very low level. At the moment, public knowledge amounts only to the very little which is extremely dangerous. The methods by which oil is found, refined and distributed are so nearly unknown to the public that they are regarded almost as mysterious. In consequence, the public is frequently misled by the dicta of "experts" and by conclusions reached from them by individuals who are unqualified to assess the real significance of most matters affecting oil.

Consider these two instances. In connection with the provision of supplies of oil for war-time requirements, I saw it stated recently that sufficient refineries to meet the petrol requirements of the war services and have plenty of fuel oil for the Navy could be established "in a few months." Those of us who have had any experience of the designing, planning and erection of refineries can place a true value on such a statement. Moreover, those who have had experience of war, with its demands for materials and its claims on man-power, realize how easily "a few months" can be extended almost into years when opposed by more urgent claims.

Another recent statement was to the effect that oil in its crude state is safer for storage than when the petrol has been extracted. I have no unkindly feelings towards the author of that statement, but I should prefer to be a long way from him if he ever puts his belief to the test by going into a crude-oil storage tank with a naked lamp.

The oil industry, I am afraid, is unfortunate in several respects. If its difficulties ended at public misinformation, none of us would have much reason to complain. Most of our troubles, however, are more serious.

Oil, as you are well aware, is a ready vehicle for taxation. It is also an essential material in modern warfare. The former attribute has been gladly turned to purpose by the treasuries of all oil-consuming nations. In consequence, prices of oil products are so increased by taxation that they bear no relation to those at which they would be sold free from taxes or duties.

Despite heavy taxation, however, consumption of the major products of oil continues to increase. The Financial Ministers of the great countries

of the world must be well satisfied with the resulting growth of national incomes. As a counterpoise to this satisfaction, however, there is the spectacle of Ministers of War worrying for the safety of their countries' oil supplies in the event of war.

The worry has spread from individuals to governments and nations. The times are unsettled. It frequently seems that peace is already in jeopardy. Hence many nations—even those whose exchequers have benefited most from imported oil—think it essential to be self-sufficient in so vital a material of war.

Here, therefore, are two conflicting tendencies, and our industry is the sport of both. We do not yet know which tendency will prevail—whether oil will continue to be taxed heavily, or whether every nation will, in peace, exclude imported oil solely because such oil may be unavailable in war.

If fear is to be the mainspring of national policies—as it may well be—the logical development would be a policy of self-sufficiency for all, and no imports of oil. The people of each nation would pay highly for synthetic products. Treasuries would find their income reduced by the amount of the revenue formerly derived from imported oil. That revenue, however, is essential to the maintenance of solvency. Taxation, therefore, would have to be imposed elsewhere. Standards of living would be depressed by higher costs for fuels and by increased taxation.

In the meantime, the oil industry would find its outlets reduced to the consumption of those countries which were fortunate in being producers. There would, of course, be a glut of oil—good oil which could satisfy every requirement of industrial, commercial and everyday life; it would be phenomenally cheap. It would give a tremendous stimulus to all forms of industry in the oil-producing countries, and it might well shift the world's industrial centre of gravity from its present place, never perhaps to return.

The present concentrations of industrial activity and population arose from the utilization of local coal and other minerals. The countries which were fortunate in the possession of those minerals became industrialized. They were soon the suppliers of manufactured goods to agricultural lands; and they prospered greatly.

What, however, would have happened if oil had been discovered before coal? It is not impossible that cheap local fuel would have caused the growth of industry in certain oil-producing regions rather than its present situations. There would, of course, have been difficulties—lack of other minerals at one point, absence of water in another, climate elsewhere. Nevertheless, most difficulties can be overcome.

It is, I think, feasible to imagine that there might have been a geographical distribution of industry different from that which now prevails. How much more feasible would be a re-distribution now or in the future.

Gentlemen, I am much indebted to our two distinguished guests for proposing the health of the Institution. We are very much honoured to have them with us to-night. I would like to conclude by reading a couple of telegrams that I received just on coming in to dinner. One is from Dr. Dunstan, who telegraphs from New York: "Best wishes for most successful Banquet. Many American friends wish to convey their respects

to you." (Applause.) I have another, a very pleasing telegram, which comes from Trinidad : " Greetings to the parent Institution, from the local branch in Trinidad." (Applause.)

Gentlemen, I will conclude by heartily thanking Sir Samuel Wilson and Sir Claud Hollis for their kind and encouraging remarks to this body. We realize we have an important task before us, and we feel that the Institution is doing really good work. It is disseminating knowledge. It is one of the joys of this body to realize that, while little differences occur amongst all industrial workers, when you get the scientists working together they speak the one language and there is a freedom of interchange of ideas which must be of lasting benefit to the industry as a whole. I thank you very much for the way you have received this toast. (Applause.)

" The Guests "

Lt.-Col. S. J. M. Auld, O.B.E., M.C. : Without guests an occasion like this would be a very sorry affair; indeed, I think if we had no guests we would have no dinner. It seems a logical conclusion, therefore, that the guests are the most important people here. That is not the way in which things are always treated in this world, because you know that even in our own families, in our own houses, it is the guest who thanks his host for the pleasant evening. I think we should reverse the order and always, as well as welcoming the guest, thank him for being present. The present order, I do not doubt for a moment, has come down to us from the days when a free meal was a free meal; but to-day, even if the free meal is wanted, it is liable to be eaten up in taxi-fares and tips before you get there.

I think the reaction of the guest on the host is by far the most important part of the business, because the host, I am sure, has marked down his guest previously as the man most likely to appreciate his new cook or his best stories, or, at any rate, the man on whom he can depend as being a good part of his audience, and, with the approbation that goes with the story, has put on his company manners. Of course, I do not want you, our guests, to imagine that when you are not here our manners are any worse. (Laughter.) I think, Sir John, I may say we are a particularly happy family. It may be because of or in spite of the diverse interests that we represent; I do not know. Anyhow, when you are not here our manners are still quite good, but they are probably a good deal duller. Then we are not thinking of the good things of life, at any rate directly, but rather of our anticlines and of our viscosities. Still, sub-consciously we must be dreaming of these occasions, for there has crept into our being a habit of calling some of our deepest and most technical gatherings—those at which we present or read or hear several papers on the same subject in one evening —Symposia; and I am informed by my classical friends that a symposium is a drinking together, accompanied by philosophical discussion.

This is the real symposium. I would rather like to call it thus : " The Eighteenth Annual Symposium of the Institution of Petroleum Technologists "—feasting, drinking, philosophy. What more can you want? And, in case the philosophy should be lacking, I will tell you that Schopenhauer stated that happiness was merely a delusion of youth and child-

hood; but, looking around here, it is perfectly apparent that Schopenhauer knew very little about symposia, still less of Annual Dinners, and nothing at all about petroleum technologists. (Laughter.)

It is with thoughts of that kind that I have risen to thank our guests for being here. Whether they are here as public men come to pay a little regard to our Institution, or as representatives of other learned and kindred societies supporting their fellow-craftsmen on this occasion, or whether they are here in their private capacities as our individual friends, we gladly welcome them, and we thank them for making the evening a success. (Applause.) I hope I shall be allowed to mention one or two of them without appearing to be discriminatory.

You have already heard Sir Samuel Wilson and Sir Alfred Claud Hollis, and I think as Pro-Consuls of Empire we appreciate very much the interest that they have taken in petroleum. In the case of Sir Samuel that interest has developed into a direct association; and perhaps we may be permitted to assume that it is the peak even of such a brilliant career to become an oil man. In regard to that, as I gather from his speech, Sir Samuel has out-done Mahomet, for Mahomet in the end had to go to the mountain, whereas the "Apex" has come to Sir Samuel. (Applause.)

It is with particularly personal feelings that I greet also the Government chemist, Dr. J. J. Fox, for Dr. Fox is a very old—I might say a life-long—friend of mine; and, Dr. Fox having comparatively recently taken over his august position, it is fitting, I think, that you should all know that he is the first civil servant to have done so. His encyclopædic knowledge and his reputation in the scientific world forced him, if I may put it so, almost literally into the high position which he at present holds. His knowledge of petroleum is almost unbecoming in one who is not a professional oil man. At least, one is inclined to think so until one realizes that he knows just as much about every subject with which he has to deal, and they are very many and very diverse. I can only hope, Dr. Fox, that your knowledge of petroleum will be used in the matter of excise, at any rate, on the side of the angels.

We have, of course, Mr. Starling, concerning whom I would like to say a few words later, but there is also another public servant, Major Cook, with us. He is the Chief Engineer of the Roads Department of the Ministry of Transport. Major Cook could, I think, teach even Mr. August Kessler something about oil economics, for the more and better he makes his bituminous roads, the more can the Government collect in the matter of road tax and petrol duty. I think in the matter of making money out of heavy residues Major Cook has the whole range of cracking processes beaten right out of sight. (Laughter.)

It is always particularly happy on these occasions to welcome the representatives of other societies, and it is an especial pleasure to us to-night to have a gathering with an international flavour in that we have with us M. de Boulard, who is the President of the Association Française des Techniciens du Pétrole. I hope M. de Boulard will take back to France very pleasant recollections of this evening, and will convey our very best wishes and kindly greetings to our colleagues, the Members of the French Society.

Then we have Professor O. T. Jones, the President of the Geological

Society. We have Mr. P. C. Kidner, of the Institution of Automobile Engineers, and Mr. H. T. Young, the President of the Institute of Electrical Engineers; and also, if I may direct attention to him, our old friend Mr. Shrapnell-Smith, who so ably and benignly presides over the Petroleum Industry Committee of the British Standards Institution. (Applause.)

To Professor Jones I would say that despite the over-production of oil in the world, geologists are still quite popular with us. To Mr. Young I would say that this is a happy occasion, because I believe this is the first one on which the President of the Electricals has dined with us. I hope it will be regarded as a precedent and develop into a tradition.

From the great oil world we have with us again Mr. J. B. August Kessler. Mr. Kessler has always identified himself very closely with this Institution, and we very much appreciate his support. (Applause.) The Institution honours itself, I think, in any honour that it can pay to Mr. Kessler, and we look forward to still closer association with him in the future.

But it is with the name of Mr. Starling that I wish to associate this toast, and I do not think there ever was a more fitting choice than to ask Mr. Starling to reply to this proposal in his honour and to his health. Mr. Starling is well known throughout the petroleum industry; he is liked and admired. We as an Institution will not readily forget the help that he gave us at the time of the organization of the first World Petroleum Congress. Had it not been for his guidance, his sagacity and his flair for coming to our help at the moments when we found ourselves in difficulties from which he rescued us, things would have been very different indeed. Then with the framing of the Petroleum Production Act of 1934 Mr. Starling, as Director of the Petroleum Department of the Board of Trade, found himself the centre of control of the Regulations framed around the finding of oil, as we hope it will be, in England. But whether it is found or not, we know that with these very wise provisions, framed, I may say—it is an open secret—practically by Mr. Starling himself, we have the petroleum industry in very safe hands indeed. That was realized, I think, also, when we saw the report which reached us in the Press of his visit to Geneva not so very long ago. Perhaps Mr. Starling has already tired of hearing of these reports from Geneva, because I think the Press in talking about it, very appropriately said "The British representative flew home." (Laughter.)

If I may be allowed to say so, Sir John, I think Mr. Starling is almost the ideal official—courteous, helpful and not merely helpful, but constructive. (Applause.) There must be in this room a good many besides myself who have sought his advice and his help, and I am certain that they, like myself, have come away very fully satisfied.

It is with the greatest pleasure that to-night I propose this toast "The Guests," coupling it with the name of Mr. F. C. Starling. (Applause.)

The toast was duly accorded.

Mr. F. C. STARLING: I am not going to weary you with a long speech, because, belonging as I do to the Civil Service, whose golden rule is that we must be seen and not heard, if there was any spark of oratory in me when I was born, it has been quite effectively killed as the result of thirty years in that Service. Our political masters quite properly do the talking,

and we are content to sit in the background and try to advise them what not to say. (Laughter.) I must say they do not always take our advice.

Mr. President, I regret very much the absence to-night of the Minister, Captain Crookshank, who I know would very much have liked to be here, but unfortunately he had a previous engagement of very long standing, and in consequence was not able to accept your invitation. If he had been able to come I am quite sure he would, as the Minister responsible for petroleum, have been able to say, from his personal experience and by reference to the large proportion of his time which is spent in dealing with oil questions, that His Majesty's Government is really alive to the importance to this country of oil supplies, whether imported or home-produced, and I am sure, sir, he would at the same time have paid his tribute to the wonderful work which the British oil industry is doing throughout the world.

While I am quite sure there are many others here who are much better qualified than I am to respond to this toast, I am going to claim that there is no one who can feel more sincerely and deeply than I do in replying to it. I am comparatively a new-comer to the petroleum industry, but during the six or seven years that I have been associated with the Petroleum Department I have received nothing but help and kindness from everyone with whom I have come in contact. Your President, Sir John Cadman, has been foremost in giving me that help. I am not an expert, and there are many questions in connection with petroleum where expert advice has been desirable, and in connection with which we have had to go outside our Department to the industry, to the Institution and to friends like Sir John Cadman to help us.

Colonel Auld said a good deal about the petroleum legislation, and, while I am very proud to have been associated with the Petroleum Department at a time when a serious effort is being made to discover whether there is petroleum in this country, I should be the first to recognize the great help we received from those in the industry and from the Institution itself in the framing of that legislation. Quite clearly it is something which, in spite of what my good friend Colonel Auld has said, we could not have done by ourselves.

I would like just to say a word about the Petroleum Department because I do not often get the opportunity of having a talk to you. I think you in the industry all know that it is one of the primary functions of the Petroleum Department to help the British oil interests in any direction in which our services can be usefully given. During recent years, when conditions in many parts of the world have been abnormal, that side of our work has been pretty heavy, and even a highly organized and efficient industry such as the oil industry, with world-wide associations, does not escape the chilly blasts which have been blowing during recent years. Anyway, the industry can be assured that the Petroleum Department is there to help, and, while one of the causes for it may be something which we all would have been glad to avoid, the Department and the industry have got to know one another very much better during the past few years.

I am sure we all agree that it is a good thing that in this country we have organizations like your Institution, engaged in a good solid piece

of work as a scientific and technical body to establish the facts in relation to the many important technical matters which arise in relation to the petroleum industry and to make available to its members and, through them, to the world, up-to-date and reliable information of developments that are always taking place.

Our scientific and technical institutions do not concern themselves with political and ordinary trade questions; and in making that remark it must not be assumed that I am disagreeing with what your President has said to-night about broadening the basis of membership of your Institution; but we are in this country very proud of these independent bodies which have got this solid job of work to do, but which do keep out of politics and the ordinary trade questions of the day, although much of the work they do is obviously of value to those who are running the commercial and other sides of the industry. I am quite sure we all agree that this work must continue. I know the leaders of this industry are helping the Institution, and I am sure we can rely on them to give the Institution all the help they possibly can.

Lady and Gentlemen, Sir John Cadman, I thank you very much for the kind way in which you have received the toast which Colonel Auld has moved. I am sure all my fellow-guests will agree that we have had an excellent dinner and an enjoyable evening. I thank you very much indeed on behalf of all the guests. (Applause.)

(The National Anthem was then sung.)

VISIT TO PORTSDOWN TEST WELL OF D'ARCY EXPLORATION COMPANY.

On the invitation of the President, Sir John Cadman, G.C.M.G., D.Sc., members of the Institution were privileged to vist the Portsdown No. 1 Well in Hampshire on Saturday October 10th, 1936. The visit was arranged on the day following the Annual Dinner, to allow members who were coming to London for the Dinner the opportunity of participating. As a result, over one hundred members were able to make the journey by train to Portsmouth on the Saturday morning, and several more travelled by road.

The visitors were entertained by the President to luncheon at Kimbell's Restaurant, Southsea. In the unavoidable absence of Sir John Cadman, Mr. C. A. P. Southwell (Anglo-Iranian Oil Company, Member of Council) presided at the luncheon. After reading a telegram of good wishes from the President, Mr. Southwell welcomed the presence of so many members from overseas. They were also particularly pleased to welcome Monsieur A. de Boulard, President of the Association Française des Techniciens du Pétrole.

Mr. Ashley Carter (Member of Council) expressed on behalf of himself and all present their gratitude and appreciation of Sir John's kindness. It was a fortunate circumstance, said Mr. Carter, that the Anglo-Iranian Oil Company, with its wide experience in oil-field development, should have been granted the necessary authorization to drill in Great Britain. It gave the assurance that the best possible knowledge and technique would be employed to carry out the undertaking. Since the days when the Hardstoft and other wells were drilled, the practice of oil-field exploration and development had made tremendous strides. Geophysics was able to supplement the work of the geologist. Equipment had improved in design, and was more efficient and economic in operation. The metallurgist had made great advances in special alloys which were now available to the prospector.

He felt sure that what they would see at Portsdown would convince them that the D'Arcy Exploration Company, the Anglo-Iranian subsidiary, had taken advantage of every resource available to ensure the success of their undertaking. If it should happen that the operations at Portsdown and other locations were not productive of the results they all ardently desired, they in Britain would at least have the satisfaction of knowing that the controversial question of the existence or absence of oil in England had been fully tested and proved in the light of present-day knowledge and equipment.

Mr. Carter concluded by reading a telegram which he proposed to send to Sir John Cadman conveying the appreciation of all present of Sir John's hospitality and wishing the Company good fortune in their venture to discover oil in England.

The visitors then proceeded by motor coaches to the site at Portsdown, about 2½ miles from Southsea.

The layout of the plant has been arranged in such a way as to take full

General View of Portsdown Test Well.

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UNIV. OF MICH.

advantage of the contours of the ground. At the highest part of the site are four bolted steel tanks, each of 12,000 gallons capacity for water storage, while immediately below these three mud tanks are sited. These latter consist of rectangular bolted steel tanks, each 40 ft. long by 10 ft. wide by 4 ft. deep, providing a total of 4800 cubic feet of prepared mud fluid.

By this arrangement a constant pressure is available both on the water and the mud fluid supply, thus obviating the necessity of pumping should it be desired to " kill " the well by the introduction of mud fluid or water.

Power is provided by four locomotive-type boilers each capable of evaporating 3600 lbs. of steam per hour at a pressure of 250 lbs. per square inch. Coal is used for firing the boilers, and here again a considerable saving is effected in coal-handling charges, owing to boilers being placed below the unloading platform from which the coal can gravitate to the bins behind the firing-platform.

A water-softening plant is installed for treatment of all the raw feed-water.

Lighting is supplied from the service mains, but in the event of a failure to the grid system an independent supply is provided by means of a 3-K.W. petrol-driven set with six flood-lights mounted on suitable tripod stands and connected up by flexible leads 100 ft. long.

The drilling plant embodies the most up-to-date gear, the majority of which has been manufactured in the United Kingdom.

Provision has been made for both rotary and percussion drilling, although up to the present the latter system has not been used. The cellar is well designed, and provides an area 26 ft. square with a height of 12 ft. from the cellar base to the derrick floor. This 12 ft. is ample to provide a working space below the derrick floor even after the casing programme has been completed and the final well-head fitted.

The derrick is 136 ft. high with a 26 ft. base, and is designed, as is all the weight-handling equipment, for a live load of over 200 tons.

Provision is made for the recording on a chart of the load carried by the bit, the table revolutions and the torque applied to the drill pipe; these records, used in conjunction with the footage charts, provide very accurate information regarding the most suitable feed and speed for the drilling bits in the various formations to be drilled.

Wherever it is practicable, standby units are provided in order to reduce to a minimum the possibility of any interruption in the work. An auxiliary hoist for the drill pipe is available in the calf-wheel of the cable-tool rig, while two main slush pumps provide 100 per cent. standby as regards the mud-circulation system.

The various drilling bits comprise the most modern types ranging from the well-known fish tail and other drag bits for soft formation, to roller cutter types for drilling the hardest rock. A comprehensive range of fishing tools designed to overcome any normal fishing job is also maintained at this centre.

IGNITION QUALITY OF DIESEL FUELS.

THE Technical Committee on Diesel Fuels of the Chemical Standardization Committee of the Institution of Petroleum Technologists have carried out a considerable amount of work in regard to the determination of the Ignition Quality of Diesel Fuels. As the result of this work they have prepared a Draft Tentative Method of Engine Test for Diesel Fuels, which is reproduced below. In publishing this draft the Committee hope that those concerned with the testing of Diesel Fuels will make use of the Method and of the Secondary Reference Fuels in experimental work, and will also put forward any comments which would assist the Committee in their deliberations.*

It is not yet possible to make a final decision regarding the Primary Reference Fuels, but two Secondary Reference Fuels have been selected, and the specifications of these are given in the Draft Method. The complete correlation of the Secondary Reference Fuels with Primary Reference Fuels is under consideration. The Cetene Number of the High-Ignition-Quality Reference Fuel is approximately 80, and that of the Low-Ignition-Quality Reference Fuel is approximately 20. Supplies of the two Secondary Reference Fuels are in course of manufacture, and will be available for purchase from the Anglo-Iranian Oil Company.

DRAFT TENTATIVE METHOD OF ENGINE TEST FOR DIESEL FUELS.

I.P.T. Serial Designation—F.O.39(T).

SCOPE.

This test is designed to cover the determination of the Ignition Quality of Diesel Fuels, excluding doped fuels.

DEFINITIONS.

The ignition quality of a fuel is a measure of the relative time required for combustion to start after the commencement of injection; the shorter the time (or delay angle) the higher the ignition quality.

The delay angle is the angle in degrees of crankshaft rotation which

* Comments should be addressed to The Secretary, Chemical Standardization Committee, The Institution of Petroleum Technologists, Aldine House, Bedford Street, Strand, London, W.C. 2.

elapses between the beginning of discernible combustion as determined by pressure rise from the compression line.

Under any given conditions the delay angle is a function of the ignition quality, which is independent of engine conditions or engine within the limits set forth below.

Delay angles in degrees of crankshaft rotation are determined by engine characteristics, running conditions, etc., and may thus vary for a given fuel over a wide range.

PRIMARY REFERENCE FUELS.

Cetene or cetane in blends with alpha-methylnaphthalene have been proposed as primary standards, but a final selection has not yet been made.

SECONDARY REFERENCE FUELS.

Any primary reference fuels are probably more affected by engine conditions and design than suitable secondary reference fuels, which are to be preferred for all routine tests.

The secondary reference fuels used shall be those designated as I.P.T. High-Ignition-Quality and I.P.T. Low-Ignition-Quality secondary reference fuels, and are obtainable from the Anglo-Iranian Oil Co., Ltd., Britannic House, Finsbury Circus, London, E.C. 2.

The High-Ignition-Quality Reference Fuel is a highly-refined Iranian gas oil produced by SO_2 treatment of straight-run gas oil having a specific gravity of 0·840 to 0·845. The complete analysis of a sample of the material, and the manufacturing tolerances, are as follows :—

	Specification Product.	Manufacturing Tolerance.
Specific Gravity at 60° F.	0·807	
Distillation :		
I.B.P.	241° C.	
10 per cent. at	254° C.	
20 ,,	259° C.	
30 ,,	264° C.	
40 ,,	268° C.	
50 ,,	272° C.	270–280° C.
60 ,,	276° C.	
70 ,,	282° C.	
80 ,,	290° C.	
90 ,,	304° C.	
F.B.P.	335° C.	Not above 340° C.
Total distillate	99 per cent.	
Residue	1 ,,	
Volume at 300° C.	89 ,,	
Aniline point	87·4° C.	
Setting point	5° F.	Not above 10° F.
Pour point	10° F.	Not above 15° F.
Viscosity at 100° F.	3·15 cs.	Not under 3·0 cs.
,, ,,	34 seconds Redwood I	

The Low-Ignition-Quality Reference Fuel is composed of a cut from SO_2 extract from Iranian kerosine. The complete analysis of a sample of the material, and the manufacturing tolerances, are as follows :—

	Specification Product.	Manufacturing Tolerance.
Specific Gravity at 60° F.	0·875	0·874–0·876
Distillation :		
I.B.P.	179° C.	
10 per cent. at	198° C.	
20 ,,	202° C.	
30 ,,	205° C.	
40 ,,	209° C.	
50 ,,	212° C.	210–215° C.
60 ,,	217° C.	
70 ,,	223° C.	
80 ,,	230° C.	
90 ,,	240° C.	
F.B.P.	259° C.	Not above 265° C.
Total distillate	99 per cent.	
Residue	1 ,,	
Flash point	138° F.	Not under 130° F.
Colour (¼ in. cell)	1·3 Y, 0·05 R	
Viscosity at 100° F.	1·66 cs.	
,, ,,	30 seconds Redwood I	
Aniline point	1° C.	Not above 2° C.
Aromatic content	61 per cent.	

REPORTING OF RESULTS OF TESTS.

All results shall be reported as Ignition Numbers, the Ignition Number being the $\frac{\text{percentage by volume}}{10}$ of high-ignition-quality reference fuel in that mixture of high-ignition-quality and low-ignition-quality reference fuels required to match the sample under test. Results shall be expressed to the nearest 0·5 number.

USE OF SECONDARY REFERENCE FUELS.

Apparatus.

Type of Engine. Examination of typical samples of diesel engine fuels has shown that the ignition quality in relation to reference fuels obtained from suitable crudes is not affected to an appreciable extent by the engine conditions used or the make of engine in which the test is made, provided that doped fuels are not included in the survey. Tests against the proposed primary standards have not yet been proved to be as independent of the engine used or of the running conditions.

A technique which relies on routine tests in terms of suitable secondary fuels has, therefore, the advantage that any type of diesel engine may be used by simple methods without risk of appreciable difference in results.

Certain hot-bulb engines have special fuel requirements, as have engines which use spark ignition for heavy oils. No form of test is suit-

able for grading fuels for these engines except direct tests in the engines themselves.

Indicator.—For the method designated "Running Test" an indicator is required with which a pressure/time or a rate of pressure change/time diagram can be taken, and this should be such that a change of one quarter of a degree of crankshaft rotation is measurable. The indicator should be suitable for determining the moment of lift of the spray valve to the same accuracy. The bouncing-pin type of indicator is not recommended.

Procedure.

1. *Running Test.* For this test the engine should be run at normal speed or, in the case of variable speed engines, at not less than one half of the maximum speed, and at a load which should be maintained constant, but which may be any desired fraction of full load giving steady operation below the smoke point.

The inlet air and water-jacket temperatures should be maintained constant to within $\pm$ 2° C. during the tests and at normal values for the engine used. The tests should not be commenced until all temperatures have become steady. The fuel-spray valve should be free from carbon trumpets; these do not affect ratings while they remain constant in size, but the breaking away of a trumpet during a test may alter the delay angle on the measurement of which the accuracy of test depends. The spray valve should lift steadily, and the load and speed should not be such that erratic opening is liable to occur with any viscosity of fuel likely to be examined.

The test is made as follows :—

With the engine running under steady conditions as specified above, run on the high-ignition-quality reference fuel and measure the delay angle in degrees and fractions of a degree. Check the readings three times and average the results. Individual readings should not differ over a range greater than half a degree.

Repeat using a blend of 80 per cent. high-ignition-quality reference fuel and 20 per cent. of low-ignition-quality reference fuel (blends by volume).

Repeat using a 60 per cent./40 per cent. blend of reference fuels and, if very low value samples are to be tested, include as many low value blends as necessary, so that a blend poorer than the poorest sample has been examined.

Plot the delay angles of these blends against the percentage of high-ignition-quality reference fuel in each blend.

Test each sample in the same manner, and from the measured delay angle of each determine its Ignition Number by reference to the curve plotted as described.

During the tests of the samples it is desirable to include two or three check tests of blends of reference fuels and, if more than a quarter of a degree change of delay is noted for the high-ignition-quality fuel, or more than 2 degrees for the low-ignition-quality fuel a corrected calibration should be made for rating further samples.

The delay angle/ignition number curve will change from day to day by small amounts and, while a curve once determined can be used as a rough guide, it is necessary for accurate work to re-determine it daily.

2. *Throttling Test while Running.* Arrange the engine with a large-diameter inlet pipe and expansion chamber about ten times cylinder volume or more and couple a mercury manometer to the expansion chamber. Fit the inlet to the expansion chamber with coarse and a fine control throttle valves, and arrange a cock in the exhaust pipe near to the cylinder.

Run the engine at normal speed, or at not less than half full speed for a variable-speed vehicle engine, and adjust the load to about $\frac{1}{3}$th full, or the load above this which gives steady running.

When conditions are steady as regards jacket temperature and general working, with the inlet throttle valves fully open, change to the high-ignition-quality reference fuel and open the exhaust test-cock. Steadily throttle the inlet air, noting the inlet system depression in inches of mercury and fractions of an inch to the nearest tenth, and, keeping the engine speed constant, note the exhaust test-cock. Continue to throttle slowly until a misfire occurs as denoted by a puff of white smoke at the test-cock. Record the depression at this point, and repeat the test three times, taking the average value.

Repeat this test for a series of blends of reference fuels and plot the average depression pressure at which misfiring occurs against the Ignition Numbers of the blends. Test each sample in the same way and determine its Ignition Number by reference to the plotted curve connecting depression in the inlet system with Ignition Number.

This method has the advantage that no apparatus is needed which cannot readily be arranged for in any test shop, but is not so accurate as the first method.

Accuracy.

Ratings determined by either method 1 or 2 should not differ by more than 1·5 Ignition Numbers from one engine type to another or between various conditions of running, and will usually be much closer than this. With an accurate indicator, method 1 should give results repeatable on a given engine and given engine conditions to within 0·5 Ignition Number, and this represents about the limit of accuracy obtainable.*

* *The aniline point* (and some similar indices) which gives an approximate indication of ignition quality may give results which differ from engine test results by an amount up to 3 Ignition Numbers for some fuels, although it is usually a good indication to about 1·5 number. It fails completely for doped fuels, fuels of vegetable and animal origin, and also for the proposed primary standards.

THEORETICAL CONSIDERATIONS ON THE MANUFACTURE OF PETROLEUM SPIRIT.*

H. Weiss.†

Increasing Importance of the Significance of Chemical Structure.

The manufacture of spirit was primarily purely a method of extraction by distillation so as to obtain molecules of a definite volatility from the crude oil. When it was found that the result of this process could no longer be controlled by means of a simple determination of density, the significance of chemical structure was first introduced.

When the demand for spirit became so great that it was no longer satisfactory to extract that which pre-existed in crude oil without dealing with objectionable quantities of distillation residues, "cracking" was investigated—in other words, a controlled pyrogenetic treatment intended to transform larger molecules into those of a desired size. These cracked spirits had several defects; they had an unpleasant odour, a colour, and easily formed gums on storage, but it was shown repeatedly that the principal part of the problem, carburation, could not be overlooked.

Similarly, a relation between the knocking tendency and the chemical structure of hydrocarbons was being realized more and more. It proved that cracked spirits seemed less detonant than those obtained by simple distillation. The cause of this was attributed at once to double bonds which were responsible for the disadvantages quoted above. The author is inclined to believe that the relative speed with which the notion of antidetonant spirit was adopted was not independent of the necessity of improving the market for cracked spirit. Perhaps the unsaturated bonds have an antidetonant action, but it is not sure that cracked spirits owe the best of their quality to them; branched hydrocarbons such as *iso*octane and cyclic hydrocarbons certainly play an equally important part.

Finally, the small molecules were considered with the aim to associate them in sufficient quantities so as to obtain always the desired size. Moreover, the cracking industry has placed on the market large quantities of unsaturated gaseous hydrocarbons. This circumstance favoured the easier method of chemical combination. However, chemical synthesis by polymerization is expensive; it is only justified if it conveys to the molecules a higher antidetonant value such that when blended with other spirits in relatively small quantities they acquire a higher commercial value. We have now fully arrived at the problem of industrial organic synthesis. To obtain a satisfactory solution it is necessary to draw attention to the general laws of chemistry.

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* Paper read at a General Meeting of the Association Française des Techniciens du Pétrole, March 28th, 1936.

† Professor, Faculty of Science, Strasburg: Director, l'École Nationale Supérieure du Pétrole.

Cracking and Structure.

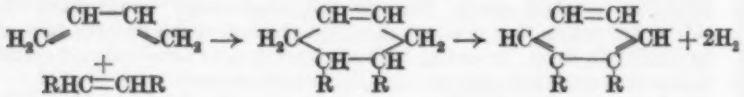
The works of Gault, Hugel and their associates on the pyrogenetic decomposition of pure hydrocarbons of known structure have shown the successive development of several types of chemical reactions which are the following, in order of increasing temperature. First, an isomerization of straight chains giving branched structures. Then a rupture of the chains takes place forming double bonds and cyclization. Finally, dehydrogenation and formation of aromatic hydrocarbons. One recognizes in these reactions the effects required in "reforming" spirit which is too rich in hydrocarbons with straight chains, a process consisting in heating them to temperatures sufficient to cause isomerizations, cyclizations and the formation of aromatic hydrocarbons.

Polymerization.

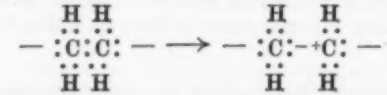
Polymerization of unsaturated hydrocarbons has been known since the beginnings of organic synthesis. It was at once seen that the possible reactions were numerous and that they followed in chain reactions. Some general laws have been sought which would throw some light on these complicated mechanisms. They were found in several lines of consideration:

(1) Morphological methods dealing qualitatively with the behaviour of the molecules or of their fragments (radicles) without considering their internal structure. Apart from the activity of unsaturated bonds which are susceptible of attaching to the molecules, the high power of combination of a radicle at the moment immediately following a chain rupture was noticed. Different authors have thus described a large number of reactions in chains which take place in several transformations. For example, the progressive transformation of ethylene molecules into aromatic molecules (according to Wheeler & Wood).

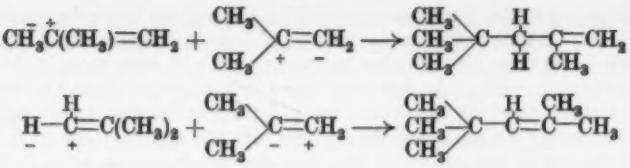
$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2$$



(2) Methods relating to the electronic theory of valency. In these, Kekulé's valency is represented by a couple of electrons which is shared by the carbon and hydrogen atoms in their peripheral shell saturated with electrons. When the rupture or the momentary separation of two carbon atoms occurs, this couple of electrons remains fixed to one of the two carbon atoms; whereby an electronegative charge appears on the one atom and an electropositive charge on the other.



Thus Kline and Drake represent various mechanisms of polymerization reactions, in particular the transformation of isobutene into isooctene.



or

Likewise, certain catalytic reactions are explained by surface influence; the mechanism of dissolved catalysts is always explained by the momentary formation of intermediate, unstable and addition reaction products.

(3) Methods relating to theories of thermochemistry. These are all derived from Berthelot's principle of the evolution of maximum heat. This principle has numerous exceptions, since it does not account for endothermic reactions. It is, however, applied implicitly in numerous cases, especially in attempts which have been made of distributing the heat of formation of molecules amongst the various exchanges of valency between atoms, and of assuming that the greatest heats of formation correspond to those reactions which are the most difficult to carry out (greatest energies of activation). For instance, the three following energies of activation illustrate, in the order of increasing temperature, the three reactions of the opening of a double bond, the rupture of a carbon bond and the dehydrogenation of a hydrocarbon.

Opening of a double bond $C=C \longrightarrow C-C + 40{,}000$ calories.
Rupture of a carbon bond $C-C \longrightarrow C + C + 78{,}000$ calories.
Dehydrogenation of a hydrocarbon $C-H \longrightarrow C + H + 93{,}000$ calories.

(4) Methods relating to the laws of chemical mechanics. These laws take into account not only the heat evolved, but also the variation in volume during the reaction. The function considered is the "free energy." The possible chemical reactions are those which cause a decrease in free energy—this is the true generalization of the second law of thermodynamics of the degradation of energy.

In order to know the free energy of a chemical system under given conditions of temperature, pressure and mutual concentration of the constituents in the fluid phase, it is necessary to know the thermochemical data and the complete qualitative data of the reaction considered, and to determine experimentally under one set of conditions all the data defining the state of chemical equilibrium. This has not been done for reactions between hydrocarbons. One is obliged to resort to Nernst's hypothesis founded on the value of the free energy of a system and on that of its derivate at the temperature of absolute zero. Considerations of this type have already been applied to mutual transformations of hydrocarbons by Von Wartenberg about thirty years ago. They were revived by Francis about ten years ago in a slightly different form. He simplified the complete equations of the free energy of reactions of the mutual transformation of hydrocarbons, and expressed the results of his calculations as values of free energy of the said hydrocarbons as a function of the temperature. A *résumé* is given in Fig. 1. The axis of abscissæ represents the free energy of the carbon and of the uncombined hydrogen molecule; the other curves refer to various hydrocarbons.

The tendency of the transformation is from the highest free energies towards the lowest. It is seen that in the vicinity of ordinary temperatures, methane is more stable than all the other hydrocarbons, and even more stable than the mixture $C + H_2$. At temperatures below a certain limit the ethylene hydrocarbons tend to transform by polymerization into more saturated hydrocarbons. Above a certain temperature the contrary occurs. Acetylene is the only one of which the free energy decreases with increasing temperature; it is seen that above a certain temperature it will be the only one which will be formed spontaneously from its elements.

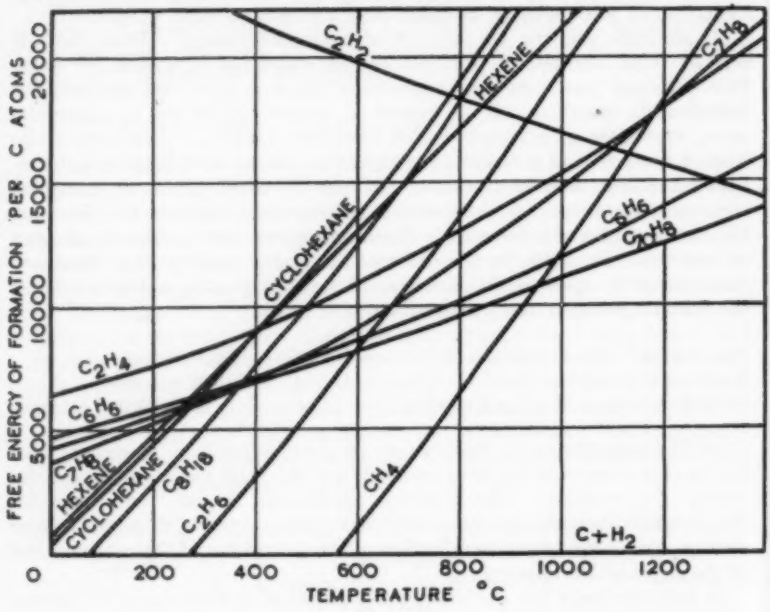


FIG. 1.

(5) Speed of catalytic reactions. The above considerations enable us to discern those reactions which are possible under the given conditions of temperature, pressure and mutual concentration of the constituents. Generally, however, passive resistances constrain the reaction, or chemical friction (according to the terminology of different authors), retards or even completely stops the transformations. Generally, when the free energy of the system is not revolutionized, an increase of temperature or pressure increases the speed of the reactions. When it is desired to carry out the reactions at much lower temperatures or pressures, it is necessary to resort to catalysts which choose one or several reactions and allow them to be carried out at an appreciable speed. If some general principles are now held favouring the "activity" of a known catalyst, empirical, only systematic experiments will enable us to find selective catalysts for new reactions.

At present three types of processes have been established industrially for the polymerization of hydrocarbons in the United States :

(1) Universal Oil Company polymerizes olefines from cracked gases at 230° C. and under a pressure of 30 kg./cm.^{2} using phosphoric acid as catalyst.

(2) Pure Oil Company treats the same initial material under conditions of heat and pressure alone : to obtain in particular, branched hydrocarbons of octane number 78–80 by operating at about 500° and 100 kg. ; to obtain in particular aromatic hydrocarbons of octane number 85–105 by operating at higher temperatures 650–725° and 10 kg.

(3) Philipps' Company is more interested in obtaining saturated hydrocarbons from natural gases. Conditions of temperature and pressure must be selected so as to effect simultaneously, cracking with the formation of active radicles and polymerization of these radicles.

Operating conditions 500–600° and 120–180 kg.

At the present time, general chemical theories enable us already to understand the chemical reactions of the processes actually used. The author considers, however, that they will play an always increasing part in the adjustment, improvement and development of these processes. The petroleum industry is becoming more and more a great industry of chemical synthesis.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Forty-seventh General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on March 25th, 1936, Commander H. V. Lavington, R.N., Branch Chairman, in the Chair.

The following paper was read :

SOME NOTES ON GAUGING AND TESTING OF CRUDE OILS.

By A. H. RICHARD, A.C.G.I., B.Sc., A.M.Inst.C.E. (Member).

The notes are divided into three parts :—

A. Expression of quantities derived from a measurement of oil in bulk.

B. A curious hydrometer fault.

C. Suggested Tank Sampling Method.

PART A.

EXPRESSION OF QUANTITIES DERIVED FROM A MEASUREMENT OF OIL IN BULK.

It is frequently found that the degrees of accuracy in successive stages in the evaluation of deliveries of oil are not consonant with each other or with mathematical principles.

This means a considerable amount of unnecessary work with no gain in accuracy.

As it may not be generally recognized how much labour can be saved by attention to significance of figures, it is hoped that the following notes may be of service, not only to those responsible for working up oil deliveries, but also to others who have to deal with multitudes of figures.

It is fundamentally unsound to carry the result of a calculation to more places than can be warranted by the initial quantity. There are many who, quite erroneously, think greater accuracy is achieved.

It must here be stressed that whilst units or measurements, errors in which can reasonably be expected to balance out over a period, may be approximated fairly liberally, any factor which has a constant bias must be taken to finer limits, which will be controlled by considerations of importance, frequency and value.

The starting point for the subject under discussion is the capacity of the storage tank, which is usually arrived at by strapping, the accuracy of which it is not proposed to criticize. There does not appear to be any

reasonable alternative, except perhaps the internal-diameter method, and it must be assumed to be correct for the purpose.

The circumference must be read fairly closely. An error of $\frac{1}{4}$ inch in a 120-ft.-diam. tank will mean about five barrels in 80,000. This is small, but will be a constant. The author considers that the nearest $\frac{1}{8}$ inch is appropriate.

Before taking the next step, it is as well to look ahead, in order to save wading in a sea of meaningless figures.

An eventual calibration of, say, barrels per inch will have to be correct to two places of decimals for a tank 40 ft. deep, to keep within the five-barrel limit above. The calculation will be taken to four places, and as in this case the result will be about 160 barrels per inch, seven figures will be needed.

As the circumference is measured to $\frac{1}{8}$ inch (0·125), the diameter need carry only the nearest three places. The square will be approximated to seven figures, four, in this case, being dropped out of further calculation.

Similar reasoning will apply in the successive stages, seven significant figures only being retained at each.

The author is of opinion that the cumulative form of gauge table, to the nearest readable gauge division (in this case $\frac{1}{8}$ inch), is the only one to be considered. An example follows :—

Feet.	Inches.	0.	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{3}{8}$.	$\frac{1}{2}$.	$\frac{5}{8}$.	$\frac{3}{4}$.	$\frac{7}{8}$.
0	0	0	20	40	60	80	100	120	140
	1	160	180	200	220	240	260	279	299
	2	319	339	359	379	399	419	439	459
	3	479	499	519	539	559	579	599	619
	4	639	659	679	699	719	739	759	779
	5	799	819	838	858	878	898	918	938
	6	958	and so on.						

The calibration determined, say 159·71 barrels per inch, is divided by eight, correct to four places of decimals. This figure is set up on the machine, one man turns the handle and the other writes. Once done, all calculation is finished, and future generations are saved endless sums and possibilities of error.

Such a table is applicable to all tanks, and is particularly valuable for varying diameters, *e.g.*, tanks with telescopic strakes, those with uneven distribution of deadwood, and horizontal cylindrical tanks.

It is to be noted that the table has been entered to the nearest barrel only.

The nearest practical dip reading being $\frac{1}{8}$ inch, or 19·96 barrels, it is recommended that deliveries from such a tank will be amply accurate if recorded to the nearest 10 barrels.

If desired, the gauge table may be written up to the nearest 10 barrels also.

Conversion to tonnage is a vexed question. Many further errors are introduced into the calculations, and it is difficult to appreciate what useful purpose is served. The author is in entire agreement with views frequently expressed that measurement by volume should be universally adopted.[1]

However, as the method is considerably used, it is as well to deal with the point.

Firstly, the author is definitely in favour of expression of Specific Gravity to three places of decimals instead of four.

The following are the I.P.T. standards for hydrometers :—

	Series A.	Series B.	Series C.	Series D.
Tolerance . .	± 0·0004	± 0·0010	± 0·0015	± 0·0020

The highest class of instrument is only slightly better than the equivalent of three places, and for all practical purposes three are sufficient.

Continuing the example above, with barrels expressed to the nearest ten, and with an oil of say 0·91 to 0·92 sp. gr. and as 10 barrels equal about 1·4 tons, tonnage can be written to the nearest unit.

For a quantity of, say, 20,000 barrels = 700,000 Imperial gallons = 2800 tons, the percentage deduction for sand and water need only be recorded to the first decimal for a series of transactions. For an isolated delivery the second decimal may be used if it can be determined to that accuracy, which is doubted.

In any event, 0·01 per cent. of 700,000 gallons = 70 gallons. Therefore gallonage to the nearest hundred is ample.

It must be noted here that this must not apply to the direct conversion from barrels to gallons, as it would introduce a constant bias in deciding what to do with the odd fifties.

In most cases, some form of distillation test is made to determine quality as expressed by a percentage of distillate.

The author knows of no test which can warrant a percentage expressed to closer than the first decimal.

Here again, gallonage of distillate to the nearest hundred is ample, as also gravity to three places.

Part B.

A Curious Hydrometer Fault.

This note refers to an I.P.T. Series A Hydrometer, which broke after about 18 months to two years of continuous service in taking crude oil gravities. It has been carefully standardized before being put into use.

These hydrometers are weighted with shot set in pitch. The break occurred as a practically plane section across the bulb just inside the meniscus of the pitch filling. The instrument had been replaced in its case apparently intact after last being used, and was found in two pieces when taken out on the next occasion.

Gravities then read with another hydrometer showed an appreciable increase on previous samples of similar oil.

Checks on duplicates of samples previously tested with the faulty hydrometer showed the increase to be + 0·0027.

Comparison against rough gravities taken by the tank gaugers indicated a gradually increasing divergence over the previous twelve months.

It was inferred that a crack had developed, through which oil could have been drawn in on immersion, the oil temperature being always lower than that of the air during the day.

It was found that two drops of oil on the emergent stem of a similar hydrometer floating in oil depressed the reading by 0·0005.

Therefore a gradual accumulation of 10–11 drops would account for the final divergence, or about 0·03 of a drop over some 375 immersions.

Oil smears inside the bulb, and slight softening and oiliness of the pitch filling, support the hypothesis. Most of the oil would, of course, be absorbed by the pitch.

The position of the crack was such that it would easily escape casual observation.

In the author's experience such a fault is unique. The corollary is that it is a wise precaution to check hydrometers of this type fairly frequently.

Part C.

Suggested Tank Sampling Method.

The method of thieving a sample from a selected depth is clumsy, messy and inaccurate.

The author proposes that a small pipe should be inserted into the tank with its inner end at the point or points from which samples are desired.

The outer end would be brought to ground or other convenient level, ending with a valve.

The predetermined volume of the pipe would have to be flushed out before the actual sample is collected.

Mr. F. G. Edmed, O.B.E., refers to possible errors in taking the temperature of samples after pulling them up through many feet of oil.[2]

The author entirely agrees, and proposes that a dial-type mercury distance thermometer inserted through the sampling tube above mentioned would completely solve the difficulty, in a very simple manner.

The bulb would project just inside the end of the tube, and the dial would be at the sampling valve.

Such thermometers can be read to ½° F. or closer if necessary. An error of more than 1° F. would, however, be within the tolerance for gravities to three places advocated in Part A. Moreover, errors in reading would balance. The error in pulling up the sample would normally have a constant bias.

The author considers that a large number of sampling points are not justified. Tests indicate that the layering effect often referred to is not of any importance. Observations of the oil surface show fairly strong convection currents.

A system of two sampling points on opposite diameters, at 0·7 of the radius from the centre, has given complete satisfaction for a number of years, the sample being drawn from mid-depth.

References.

[1] McConnell Sanders, J., "Measurement of Oil in Bulk," *J.I.P.T.*, 1934, **20**, 665–688.
[2] Edmed, F. G., *ibid.*, p. 675.

DISCUSSION.

Mr. J. D. Fullerton agreed with the author's statement that the method of thieving a sample from a selected depth was clumsy, messy, and inaccurate, but thought there were many difficulties in the adoption of the proposal that a small pipe should be inserted into the tank with its inner end at the point or points from which samples were desired. A tank was not necessarily filled to the same height each time. There were normally two methods of taking samples: one of the top, middle and bottom, and another from the middle only. In the latter case the sample is taken from midway between the top gauge and the bottom gauge. As that was a varying factor, the tank in some cases being filled to as near the top as possible and in other cases not more than half full, the speaker failed to see how it was proposed to attain the desired end without a multiplicity of small pipes. He invited the author's explanation.

Mr. W. J. C. Cooke quoted the author's statement that he considered a large number of sampling points were not justified, as tests indicated that the layering effect often referred to was not of any importance. He agreed with the statement in regard to thin oil, but certainly not with reference to a really heavy oil. They had proved by taking a large number of samples from tanks—particularly where water was in suspension—that stratification occurred, sometimes showing differences up to 5 per cent. in the water content of the different samples, but, of course, these occurred only occasionally.

He quite agreed with the author about the advantages of measuring oil by volume rather than by weight, and mentioned that a rather interesting point in this connection came out some years ago. (W. Möller-Fernau, "Discrepancies in Calculating Petroleum Cargoes," *Petroleum Times*, April 6th, 1929, p. 589). From this and other sources it was found that there were at least eight different values relating to the definition of a cubic foot in terms of weight, and thus many different results, in tons or pounds, could be obtained from the same bulk of oil.

It has been noticed that the specific gravities of many samples were reported with a constant end figure, either 0 or 5, in the fourth place; obviously a laboratory approximation, and indicated that the gravity was not actually read to the fourth place.

The speaker asked the author if he had had any experience of the accuracy of gauging tanks with floating roofs.

Comdr. H. V. Lavington, referring to the last paragraph of the paper, asked the author whether he had had any experience of sampling tanks into which oils with a considerable difference in gravity had been pumped at various times. In such cases it seemed possible that samples drawn only from mid tank, as suggested, might not be truly representative of the average content of the tank.

Mr. A. H. Richard, in reply, said that it has been proved on many occasions that the middle sample was fully representative of the quality of the oil in the tank, and that there was little variation with depth.

The sampling method suggested would be most applicable to the majority of cases where the tank was filled to within a foot or so of the same high gauge every time.

The sampling tube would be set at mid height between average high and low gauges, and a difference of ± 6 inches or so due to varying filling levels would be immaterial, and as accurate as reaching the same point with a thief.

Mr. W. J. C. Cooke interposed saying that with gasoline tanks they had used a swing-pipe arrangement which they raised or lowered.

Mr. A. H. Richard, continuing, stated that he was going on to suggest a swing sampling tube to meet such cases as Mr. Fullerton had mentioned. The distance thermometer capillary should be sufficiently flexible to follow the movements of the swing.

He had had no experience of tanks with floating roofs, but did not see that the accuracy of gauging should be affected.

In reply to the Chairman, the author stated that he had had a limited experience of blending a light gasoline into crude oil tanks. Distillation tests on middle samples agreed quite reasonably with calculated values.

On the Chairman's proposal, a very hearty vote of thanks was accorded the author for his paper, and the President and Members of the Apex Club for the use of their rooms.

EDUCATION AND TRAINING FOR THE OIL INDUSTRY.*

By Prof. A. W. Nash.

SYNOPSIS

The author points out that the remarkable growth of the petroleum industry has caused the proper training of personnel to become of increasing urgency. Modern developments have led to the utilization of geologists, geophysicists, production engineers and chemical engineers, so that the petroleum industry requires its technical men to have had a specialized vocational training. It is observed that petroleum technology cannot be taught as a " top-dressing " to other vocational subjects with any degree of success. The author sets out the main lines for the study of petroleum technology, which should lead to specialization in one of the three main branches of the industry—geology, production, or refining. Such specialization, however, could only be satisfactory when based on a thorough knowledge of the fundamentals of physics, mathematics and chemistry, and of the general principles of engineering and chemical engineering. An account is then given of the ground to be covered in these subjects, and insistence is laid on the necessity for teaching the student to apply his knowledge, to use the literature to find new information and to interpret and use it for the solution of difficulties. In conclusion, the author remarks that in the petroleum industry the qualified graduate will find one that is unequalled in its capacity and in the opportunities of advancement offered to enthusiastic and properly trained men, an industry, moreover, which has the advantage of having been developed from its early days upon true scientific lines.

Introduction.

The remarkable growth during recent years of the petroleum industry, both in size and complexity, has caused the proper training of personnel for recruitment to become of increasing urgency and importance. Although the modern petroleum industry had its origin only some seventy years ago, it has now become a major industry of the world, producing at the present time over 200 million tons of oil per annum, as compared with some 100 million tons fifteen years ago and 60 million tons in 1912. The same period has seen the development of the modern motor vehicle, the aeroplane and the motor-driven ship to their present commanding position; there are, for example, over thirty million motor-driven vehicles on the roads to-day. The dependence of these upon petroleum supplies has led to an ever-increasing demand for this commodity, which is out of all proportion to the actual increase in the world production of oil, and it is obvious that, of necessity, every resource of modern science has had to be employed to keep pace with the demand.

In the search for oil-bearing strata the application by the geologist of physical and mathematical reasoning to the study of underground conditions has crystallized in the modern science of geophysics. The development of a new technique in metallurgical engineering has become

* Paper read at the Chemical Engineering Congress of the World Power Conference, 1936.

essential now that wells are being drilled in oil-fields to depths until recently thought to be impossible; to-day, for example, such wells may exceed 12,000 feet in depth. The control of the underground flow of oil to the wells, and the separation of gas from the oil as it is received at the surface, have necessitated the extensive application of physics to the problems of petroleum production. Particularly in the refining of the crude oil to produce the various marketable products now available, has science played a most important part; a noteworthy development in this respect may be instanced in the art of cracking, whereby a crude oil is now made to yield more than twice the quantity of petrol it contains in the natural state.

It may be truly said that to-day developments embracing the utmost economy in the cost of drilling, production and refining, have, of necessity, led to the inclusion on the staffs of the larger petroleum companies not only of highly skilled geologists, geophysicists, production engineers and chemical engineers who have specialized in petroleum technology, but also of physicists and chemists with research qualifications in the science.

Technical Standards of Instruction.

Thus it will be seen that the modern petroleum industry demands of its technical men a far higher standard of knowledge and training than formerly sufficed. Respect for physical vigour and prowess, good manners, public spirit, self-restraint and a training in the responsible use of freedom, although still important ideals, are no longer considered to be the chief qualifications necessary for those who wish to enter the petroleum industry; neither is a liberal education alone a sufficient foundation upon which to build practical experience. Specialized vocational training is now essential, and it is with this professional training that the present paper is most concerned.

One of the more fascinating aspects of petroleum technology as a profession is to be found in the breadth of the interests to which it appeals. To quote the words of Sir Thomas Holland in his presidential address to the Institution of Petroleum Technologists in 1926: "The geologist, the engineer and the chemist alike are needed in its manifold ramifications, and a grounding in all three subjects will show the trend of the student's inclinations and indicate the special lines to be pursued in his professional career."

Nature of Training in Petroleum Technology.

Speaking as one with experience of the practical side of all branches of the petroleum industry both at home and abroad, together with over thirteen years' service as a university teacher in the subject, it is the writer's considered opinion that the subject of petroleum technology is not one which can be taught as a "top-dressing" to other vocational subjects with any degree of success. Four years' undergraduate training in this subject, embracing a thorough grounding in the fundamental sciences of physics, mathematics and chemistry, together with engineering, and, of even greater importance, training in the application of these principles to the specialized and frequently complex problems encountered in the petroleum industry, is almost essential for those men desirous of becoming petroleum tech-

nologists and of obtaining, after some experience in the industry, the higher executive appointments. Those who would attain the highest rank in their profession would do well to follow a post-graduate course of some two or three years in original research, provided they show the requisite aptitude for such work.

Unlike technical schools, whose function it is to teach as many students as possible as much knowledge as they can absorb, the standard of a university school is not to be judged by the number of students it may turn out but by their quality and, to a lesser extent, by the amount of original research work it may put forward. Although known to all university teachers by experience, the lay public does not commonly understand, or fails to realize, that the higher the grade of the post-graduate work, the higher and better will be the work all through the undergraduate period from beginning to end. It may be said with truth that it is not the undergraduates but the post-graduates who set the standard throughout. As Sir Charles Grant Robertson, the Vice-Chancellor of the University of Birmingham, has said, a university school without a strong body of post-graduate workers would in reality be little better than an aggregate of glorified sixth forms, under the pitiable delusion that they were doing "university work."

Before consideration is given to the nature and extent of the necessary training, it should be understood that prior to a decision being made that a young man should enter the profession of petroleum technology, he should show an aptitude for mathematics and the other natural sciences as well as an inclination for mechanical contrivances. It is desirable that he should be able to set forth clearly and logically his views on any problems he may have to consider. In addition the possession of a good physique and enjoyment of robust health are of some importance, since in addition to the strenuous nature of his profession, the earlier part of his life may possibly be spent in tropical climates.

Ground Work.

The student of petroleum technology will eventually specialize in one of the three main branches of the industry—geology, production or refining. It cannot, however, be too strongly emphasized that such specialization can only be satisfactorily undertaken when the student has acquired a thorough grounding in the fundamentals of physics, mathematics and chemistry, and in the general principles of engineering and chemical engineering. Such knowledge is essential if a proper understanding of the specialized branch selected is to be obtained, and if the problems later met with on the field or in the refinery are to be attacked from the correct standpoint. Specialization, moreover, must on no account involve neglect of the remaining branches of the industry. A thorough knowledge of the basic principles underlying these is absolutely essential if a clear conception of the relationship of any problem encountered, to the industry as a whole, is to be obtained. The ability to visualize this aspect is of the highest value.

The primary education for a student who intends to become a petroleum technologist will not, of course, differ appreciably from that required for

any other profession, up to the age of about fourteen years. After this age it is necessary that the standard of knowledge requisite for admission to a university be attained. The later technical instruction of the student must be based on a sound general scientific training; mathematics, including the calculus, physics, chemistry and possibly mechanics, should be studied as specialized subjects, whilst the inclusion of one or two modern languages will be of advantage. The fundamental instruction in these subjects should be received either during the last years at school or during the first year at the university, before the student is permitted to proceed to his more professional training. He will then be in a position to commence this training after passing his intermediate examinations at the end of the first year.

If the student has successfully passed the Higher Schools Certificate Examination, with mathematics, physics and chemistry as principal subjects, an exemption is granted from the first-year studies at the university. Those students who have passed the Matriculation Examination only must proceed to the first-year course.

Course of Instruction in Petroleum Technology.

The work of a petroleum technologist may cover all the branches of engineering, civil, mechanical and electrical, and each of these must receive as intensive a study as the period available will permit.

In civil engineering, the design and construction of railways, harbours, roads, drainage, etc., should not be excluded from his studies, and will, of course, be augmented by acquirement of a sound knowledge of surveying in theory and practice. A thorough understanding of drawing, plan and design, should be attained from instruction in this subject, particularly from the preparation of plans at the completion of preliminary survey work.

In mechanical engineering, the operation of all kinds of steam and hydraulic plant and mechanical appliances should be perfectly familiar to the petroleum technologist. He should be able to calculate the strength of the various parts necessary to withstand whatever stresses are set up in these during operation; he should be capable of producing detailed drawings of all parts and be familiar with the processes carried out in the foundry, smithy and fitting shop. As much practical work as possible in these departments should be given to enable the student to grasp the importance of each operation.

In electrical engineering a sound knowledge of electric motors, switch gear and electrical instruments for measuring purposes is absolutely essential. Although differences of opinion still exist as to the best lines on which engineering training should be carried out, authorities are agreed that a considerable period must be devoted both to the practical and the technical aspects. In order that the necessary ground may be covered the studies must be continued throughout the period allotted for the university training of the petroleum technologist: much of the practical work is done in the vacations.

The foregoing work requires a sound knowledge of mathematical principles as well as of the calculus, and mathematics must, therefore, be studied in conjunction with the engineering subjects. The period over which this is

taught may vary with the different universities, but very advanced mathematics will certainly not be necessary. It should be sufficient if the student has a good working knowledge of the calculus and of the general application of mathematics to practical problems. The time devoted to this should not exceed two university sessions.

Sufficient knowledge of the fundamental principles of physics should also be obtained during the two years' study and, although the subject may be of very great value in subsequent studies, it is not generally necessary to proceed further than these fundamentals unless the specialized work later undertaken renders this necessary.

With regard to geology, the petroleum technologist who is not specializing in this branch of the industry should obtain sufficient knowledge during two sessions to enable him to understand the problems peculiar to this particular branch. Practical work should, of course, be undertaken to assist the student to understand and apply his theoretical training.

The geological course should cover stratigraphy, palæontology, with special reference to the micro-palæontology of the Tertiary period, and mineralogy. It is essential that the student should be conversant with the geology of the world's oil-fields so that he may have some knowledge of the areas to which he may be sent and to enable him to investigate new areas.

A knowledge of the heavy minerals will enable the strata in certain areas to be correlated, and this subject should, therefore, be given some attention.

Practical experience in geological surveying is necessary. These surveys may be carried out in the vicinity of the university or in specially chosen areas throughout the country, and the more varied the area the more extensive will be the practical training.

A recent development of geology is geophysics, and every geologist should possess some theoretical knowledge of this subject. Geophysics is an application of physical measurements, seismic, gravitational or electrical, to the sub-surface strata. The systematic use of geophysical methods as an auxiliary to geological surveying in oil-field exploitation is widespread, and even if the student does not follow geophysics as a profession, a knowledge of it will enable him to read more intelligently the reports of such surveys.

The geologist should be conversant with all the modern methods of well surveying, since the problems connected with this practice are intimately linked with the work of the geological department. This subject must, therefore, be included in the course.

Chemistry, up to the intermediate standard, is studied during the first year, and the student should then be in a position to proceed to the study of those aspects more intimately connected with petroleum technology. Three years' study in this subject is required if the student is to become familiar with the chemistry of petroleum, and of refining operations, and with the chemistry of the necessary analytical tests carried out upon petroleum products.

During the second year it is necessary for the student's knowledge of chemistry, physics, mathematics, surveying and mechanical engineering to be carried further, while additional subjects must be included in his course. The introduction to the production and refining branches of the industry can now be added, together with the fundamentals of geology and

electrical engineering. Additional instruction in workshop practice must also be given to complete the work commenced during the first year.

On the completion of the second-year course the student should have received an insight into the industry with which he has cast his lot. Although the work carried out during this year is of an elementary character, it is of the utmost importance if the succeeding curriculum is to be fully understood.

As has been mentioned previously, at the end of this year sufficient instruction in mathematics, physics and workshop practice will have been imparted to enable the student to continue his studies in those technical subjects in which such knowledge is essential. There should be no necessity, however, to continue the theoretical study of mathematics and physics further than this stage.

During the next year civil engineering should be added to the syllabus, so that the student will now be receiving instruction in the three branches of engineering together with surveying, geology and the two professional subjects concerned with production engineering and oil refining. The subjects now being studied, together with those dealt with in the first and second years, serve principally as a basis for the work to be undertaken during the fourth year, in which particular attention is paid to that branch of the industry which has been found to appeal in the highest degree to the student.

The distinction made between the production and refinery branches should be as slight as possible, so that all students will receive essentially the same course. Only in the amount of work in the chemistry laboratory should these courses vary, but in either case, if it is possible, students for both branches should be required to spend the maximum time available in laboratory work. It is then possible for an estimate to be made of the manipulative skill of the student, and of his aptitude for later work involving original research. A thorough knowledge of the standardized tests for testing petroleum and its products, both in theory and practice, is essential.

Specialized training in the refinery branch of petroleum technology is concentrated in instruction in those chemical engineering unit operations used in refining practice, such as distillation, extraction, fluid flow, heat transfer, etc. Before receiving tuition in this subject the student will, of course, be familiar with the chemistry of all refinery operations from his previous chemical studies. The specialized theoretical instruction now given should aim at a series of lectures on representative chemical engineering unit processes proceeding to the design, construction, and operation of certain equipment. At the same time the student should study such individual operations in the laboratory, and gain practical experience with both laboratory and semi-technical scale equipment. It is equally important that he should have experience in devising new refinery processes and opportunity for studying these processes for technical soundness and economic feasibility. Only by this means is he able to view the individual operations in their correct relation to each other and to the whole refinery process. The success of this training depends largely on the soundness of the previous fundamental instruction in physical chemistry. Without a sound knowledge of physical chemistry the student will not derive much benefit from this type of instruction, and it cannot be too strongly

emphasized that the previous chemical instruction given should include a thorough grounding in the quantitative aspect of chemistry. As far as possible this specialized course should be supplemented by vacational experience in refineries, where the student should gain an insight into actual works routine and technique, and also the type of problems and emergencies that arise, together with some experience in handling labour. The preparation and reading of undergraduate papers in open meetings and the opportunity to hear and discuss papers by external lecturers, each a specialist in his own particular sphere, is now of value.

Application of the Student's Knowledge.

It is extremely important that at this point the student should be taught to *apply* his knowledge, to use the literature in order to find new data and knowledge, to understand and interpret this new information and to use it for the solution of difficulties. Learning a mass of facts and principles is not the way to learn to solve problems. The student must be taught to analyse a variety of problems and situations, taught to see what data and principles are needed for a solution, guided in the discovery of such data and in the use of judgment in their selection. In short, the student should be taught how to use his previous training, experience and knowledge in order to solve difficulties and problems.

Practice in the use of field equipment is most advisable, and should be sought whenever possible. If full-scale drilling rigs are available, all students should be given the opportunity to handle them to give them confidence and to enable them to familiarize themselves with apparatus and equipment they may supervize when they join the industry. Many of the problems encountered on the oil-fields will, of course, be beyond the scope of this practical work unless vacational visits to oil-fields are possible. Production problems, for example, cannot be examined on account of the lack of petroliferous strata and formations, but drilling, fishing and casing problems can readily be examined in whatever terrain the hole is being drilled. Through such instruction and practice the work to be carried out by drilling crews on the fields can be thoroughly understood; such knowledge is of inestimable value to the student who will eventually take his place as a petroleum engineer in the fields.

A most important section in the training of a petroleum technologist lies in the examination of the methods adopted in the search for new lines of advance in technical methods. Original research is, naturally, outside the scope of the undergraduate course of training, but during the final year, when the student is concentrating on the subject in which he wishes to specialize, opportunity should be given him to spend some time in assisting the post-graduate workers engaged on various problems of research. By so doing the student is able to investigate the manner in which such problems are approached, and so equip himself to some extent for work of a similar nature which he may be called upon to undertake in the future. It is obvious that the amount of work of this nature that can be carried out during the fourth year is limited, but it should be sufficient to enable a student to decide whether or not original research would appeal to him, and the tutors to decide whether the student is fitted for such work.

The course of study outlined for the training of a petroleum technologist has been designed not only to inculcate in the student a sound knowledge of the fundamental principles upon which the present scientific status of the industry is based, and of the lines along which it is being developed, but also to bring out those inherent personal characteristics so essential to anyone entering the profession of petroleum technology. The curriculum must of necessity be a long one, by reason of the manifold ramifications of the profession, but with hard work and attention to detail it is not an unduly difficult one.

The Career.

Upon the successful completion of the course of training chosen, the qualified graduate will find ahead of him an industry unequalled in its capacity and in the opportunities of advancement offered to enthusiastic and properly trained men, an industry, moreover, which has the inestimable advantage of having been developed and directed from its early history upon true scientific lines. Young men of initiative with a desire to travel, and having powers of organization and administration, and with ability to lead, have found that the petroleum industry offers them scope for assuming a considerable degree of responsibility and, in addition, may afford them no inconsiderable amount of adventure.

SOME CHEMICAL AND PHYSICAL CONSIDERATIONS INVOLVED IN THE CEMENTING OF OIL WELLS.*

By A. Reid, M.A., B.Sc. (Associate Member).

Attention to the mechanical details of a cementing operation is one of the most important functions contributing to its success, but this may be rendered abortive by lack of foresight in the selection of the cement to be used. There is a general but mistaken idea that any construction cement is good enough for oil-well cementation, and this is possibly responsible for many failures.

The requirements of oil-well cement, the conditions met in use, are briefly outlined, and the factors effecting setting and hardening of the cement for the successful issue of cementing operations are discussed.

A brief outline of the manufacture of cements such as :—" Portland," " Aluminous or ciment fondu " cements, " Dr. Fox's Ciment Fondu " and Eisenportlandzement was given, and emphasis laid on the fact that, as different cements are used, opinions vary on the essential qualities of oil-well cements. The expectations of the cement to be used in relation to " Setting " and " Hardening " are discussed. A short explanation of these terms is given.

When cement is mixed with water to form a paste or slurry it thickens as time passes until it cannot be moulded or pumped. It is then said to have " *set*," and the time taken to reach this state is the " *setting time*." As time proceeds, the mixture acquires strength, and is said to be " *hardening*."

The times and rates respectively may vary, and may be classified as follows :—

(1) Slow setting and slow hardening.
(2) Slow setting and rapid hardening.
(3) Rapid setting and slow hardening.
(4) Rapid setting and rapid hardening.

The question arises, What type is best suited for oil-well cementing? Much depends on the actual conditions existing. The writer confines his remarks to cements used for average 4000 to 5000-foot jobs in Burma.

Cement must not acquire set in a shorter time than that required to place it. Ultra rapid-setting cement is out of the question; on the other hand, very slow-setting cement is more sensitive to underground influences of gas, oil and water. A cement slow in setting may leave a margin of safety as far as time of placement is concerned, but it is not altogether satisfactory if subject to destructive influences underground. The setting time is also affected by the concentration of the slurry and the underground temperature.

After many tests in the laboratory it was decided that for 4000 to 5000-

* Précis of paper read before the Burma Branch of the Institution of Petroleum Technologists on May 10th, 1935.

foot jobs a mixture of 40 parts by weight of water to 100 parts by weight of cement showing a set in 2 to 2½ hours at 100° F. would be satisfactory. Cements showing set in 3½ hours under the above conditions have been successfully used, but do not give such good results when active water-sands have to be shut off.

The decision between slow- and rapid-hardening cement is easy to make, as the sooner a cement acquires strength and becomes impermeable after placement, the better. Although average Portland cement has a satisfactory rate of hardening, it has been found that rapid hardening is desirable for that part of the column placed in the neighbourhood of the casing shoe. A tentative specification for oil-well cement given at the World Petroleum Congress is :—

Grout to be used in testing, 40 parts water to 100 parts dry cement.

	Tensile strength.
After	Lbs./sq. in.
1 day	250
3 days	350
7 days	425

The one-day figure is the most important. Some cements pass the three- and seven-day tests, but fail on the one-day test. Other things being equal, these cements are more likely to fail. This is the experience in the Burma field.

It is of interest to note that the one-day strength of 40 per cent. grout is practically the same as the three-day strength of a 50 per cent. grout. The reason for this is not apparent, but has been observed in many cements.

Ageing of cement may influence its properties, and if the cement is not kept in air-tight drums, changes take place progressively with time. The most important changes are the slowing up in the setting time and the rate of hardening. The latter is of some little interest; but, given sufficient time, the cement will attain practically the same strength as fresh cement. If it is accepted that the one-day strength is important in oil-well work, then the effect of "ageing" may spoil the chances of a successful cementation.

The setting and hardening properties of cement can be modified by treating the grout. Diluting the grout will slow up the setting time at the expense of the ultimate strength. Calcium chloride, used in proprietory substances as Quickset, Konset and Dehydratine, speeds up the rate of hardening. Its use is so general that a more detailed reference seems necessary.

Finely ground cement clinker has an almost instantaneous set. Manufacturers therefore add ground gypsum to the clinker to lengthen the setting time. Calcium chloride in very small quantities has the same effect, and its use in clinker meal is frequently proposed, but with a gypsum-containing product, as Portland cement, we find that calcium chloride shortens rather than lengthens the setting time. Thus a 50 per cent. grout with ordinary water may require 3¾ hours to set, whereas with a 3 per cent. solution of calcium chloride the setting time is just over 2 hours. Further calcium chloride increases the rate of hardening.

The following is a typical comparison:—

Gauged with distilled water	Gauged with 3% calcium chloride.
260 lbs./sq. in.	307 lbs./sq. in.
326 "	356 "
197 "	240 "
213 "	241 "

Calcium chloride merely affects the rate of hardening, and only very rarely increases the ultimate strength. In other words, calcium chloride may help to attain in one day as much strength as water-gauged cement attains in two days; but if similar gauging were tested after, say, three months, there would be very little difference in strength.

Objections have been raised to the use of calcium chloride as cement gauged with it may, after a period of, say, a year or so, show signs of deterioration and disintegration. The fact that the A.S.T.M. have a specification for the use of calcium chloride in cement indicates that this opinion is not general. The writer knows of no isolation failure due to the use of Dehydratine. In the laboratory, test-pieces with Dehydratine maintained below water for three months have shown very slight decrease in strength.

Little is known of the reason for the accelerating action of calcium chloride. It is known that calcium chloride picks up water from air and a number of liquids, and the assumption is that when mixed in the cement slurry it extracts water from the mass, thus allowing the cement grains to combine quickly together with such water as remains free. This view is erroneous, as Kuhl has shown that many substances not possessing the power of picking up water have a very active effect in accelerating setting and hardening.

It is not so easy to slow down the rates of setting and hardening as it is to accelerate them. One might add gypsum, as the manufacturer does, but there is a very definite limit, as excess tends to make the cement unsound. Dilute sulphuric acid might be used, as it combines with lime to form gypsum, but this does not commend itself to oil-field operators. Sodium phosphate, amongst others, has been suggested, but no really satisfactory substance has been found. It appears best for the oil-well cementer to keep two types of cement, one slow setting for deep wells and one rather less slow setting for wells of 4000 to 5000 feet, or to use only slow-setting cement, and to regulate the rates by careful use of calcium chloride. It is more convenient for the manufacturer to turn out slow-setting cement by using more iron oxide, relative coarse grinding and the addition of gypsum, than for the oil-field operator to experiment with the final product.

We now pass to factors exerting an influence underground, such as :—

(1) Temperature.
(2) Pressure.
(3) Motion of slurry.
(4) Underground water contacting/mixing with the cement.
(5) Oil and gas contacting/mixing with the cement.
(6) Muds contacting/mixing with the cement.
(7) Formations with which the cement is to bond.

Temperature has relatively more effect on setting time than on hardening rate. The higher the temperature the less time required for setting. A cement grout setting in 210 minutes at 100° F. may set in half that time at

150° F. In view of the high temperature ruling underground, its effect on setting time should be studied when fixing the grout to be used. The chief difficulty is to find the temperature at which the cement actually sets. In the course of the job the cement passes down the casing, gaining heat, and then up behind the casing, losing heat. It may be taken that the cement never actually acquires bottom-hole temperature during its passage through the well, and only that part of the grout placed round the shoe will really come to that temperature. A purely empirical but useful and reliable method of determining experimentally the grout to be used has been developed in Burma, as follows :—

The circulating mud temperature is carefully observed, and 10° to 12° F. added. This is taken as the well temperature, and the test made at it; the temperature being maintained from start to finish of the test. The result gives a very reliable indication of the time in which the first part of the grout will acquire set, and thus the time available for mixing and placing it.

Much less attention has been paid to the study of high-pressure than to high-temperature-effect on the setting time of cements. A certain amount has been done by Tickel in the U.S.A. and by Korepanoff and Muchinsky. Pressure reduces the setting time to 25 per cent. normal. The most important point is that the percentage reduction is much the same from 400 to 2000 lbs./sq.in., so apparently it is more pronounced in very deep wells than in those 2000 to 3000 feet deep.

Cement slurry in motion does not begin to thicken to set point so quickly as a still mixture, but when it does, the action of set is very rapid. This is extremely important in oil-well cementing operations. When cement begins to thicken, any agitation is likely to prevent setting to a coherent mass, so the quick acquisition of rigidity makes it imperative that slurry should be placed before the final thickening commences. It is true that part of the cement may be disturbed after taking its initial set and still form a coherent mass; but it is doubtful if pumps could move it, and such movement is not recommended. These remarks indicate that motion of the slurry lengthens the setting time; but to what extent is uncertain, as very little work has been done on this subject.

Cement in a well may either be diluted by well water or have to set under it. Dilution lengthens the setting time and reduces the final strength. Dissolved salts in the well water may enhance these effects. If excessive dilution takes place the cement will not set to form a firm mass, and becomes useless for isolation purposes. Statistics are not available showing cementing failures due to dilution with underground waters. In many cases some part of the cement at least sets in contact with well water. What effect do soluble salts have on the setting and hardening of cement? In Burma and India, sodium chloride is found in well waters. The average soluble salts in Yenangyaung and Singu waters is 4 lbs. per barrel, of which 2–3 lbs. is sodium chloride. Investigations have been carried out by various workers of the effect of salt on the setting and hardening of cement, with no concordance of results. Dr. Evans and the writer found the setting time slightly shortened, Wren found it lengthened, and more recent work in Russia appears to agree with the former. The effect of salt on the hardening of cement is interesting. The first 6–7 days are normal, then there is a loss of strength up to the twenty-eighth day, when the loss becomes negligible

and the strength remains practically constant. If the salt solution is continually renewed, the loss of strength is very marked until the cement crumbles. Crumbling is accelerated by pressure. Next to salt, sodium carbonates, as soda ash and washing soda, are the most important salts in Burma well waters, as much as ¼ to 2½ lbs. per barrel being found. Dr. Evans has shown that soda ash in the above concentrations does not adversely affect the strength of cement set under it, and the setting time is only slightly shortened, except when the cement is grouted with it, when the setting time is accelerated.

Sulphates, as sodium or magnesium sulphate, are present in some Burma waters, 1 to 2 ozs. per barrel in Yenangyaung and ten times this amount in Singu. Under certain conditions Candlot's salt or "cement bacillus" is formed with an ultimate breakdown through contact with sulphates. Aluminous cements are reported to be highly resistant to the attack of sulphates.

Generally the effect of well waters in Burma on cement is not very serious, except where dilution and/or agitation takes place.

Average cements set and harden under oil if sufficient water is used in mixing. Sulphurous compounds in oil affect the cement in a manner similar to the sulphates. Burma crudes do not markedly affect the setting and hardening of cements. Agitation of fluid cement by oil may prevent a satisfactory set. Agitation by gas has a very marked deleterious effect, and if set takes place, the cement is porous and of low strength. Agitation of cement by gas with a large proportion of carbon dioxide accelerates the setting time.

Cement, if undisturbed, will set in an atmosphere of natural gas, but the presence of sulphur compounds may affect the set of the cement; but only possibly on the surface, and not throughout the mass.

It is desirable to mud off, even temporarily, oil and gas sands before cementing.

Some of the cement will contact with rotary mud. A small quantity of mud will not affect the strength of the cement; but an appreciable quantity is undesirable, and may be extremely prejudical to a successful cementation, especially if it contains soluble salts. When mud is treated, to reduce its viscosity, with, say, waterglass, which accelerates the setting time of cement, it is advisable to precede the cement slurry with a small volume of untreated mud.

Cement will bond better with some formations than others. Little work has been done on this subject; but certain experiments indicate that sandstone gives a better bond than shale. This may or may not be a general rule. In gypsum-bearing formations there is a possibility of forming "cement bacillus" mentioned earlier. German writers stress this possibility, but the writer is doubtful if such would occur in Burma.

The above notes will indicate that some consideration should be given to the cement and grout used for cementation, as well as to the mechanical equipment or to repeat the words of Rakestraw and Parsons :—"There has been a great improvement in cementing practice since cement was first used to exclude water from oil-wells, but the improvements have been practically all mechanical, It is now time that we investigate the behaviour of the cement itself."

ON THE EFFICIENCY OF RECTIFICATION COLUMN PLATES.*

By Prof. Dr.-Ing. EMIL KIRSCHBAUM and Dr.-Ing. C. A. ANDREWS, A.M.I.Mech.E., A.M.I.Struct.E.

SYNOPSIS.

It was ascertained that the rate of change of liquid concentration during its flow over a rectification plate varied, and that the greater part of the fraction volatilized from the liquid was removed during the earlier part of the flow. The results of a series of tests on liquids of different ethyl alcohol–water concentrations are given in the form of typical travel–concentration or concentration gradient curves.

These curves indicate that a modification should be made to the assumption that the volatile fraction removal gradient is a straight line. They show that the mean concentration of the liquid on a plate is not the arithmetical mean as deduced from liquid samples taken at the entrance to, and the exit from, the plate. The true mean concentration can be found by taking into account the shape of the travel–concentration curve applicable to that plate under the working conditions for which the curve was obtained. This can be done by ascertaining the area under the curve by means of a planimeter.

On the basis of the mean concentration so obtained the real or actual efficiency of the plate is calculated.

Mathematical symbols used :

x_D = Content of more volatile fraction in the distillate, mol. per cent.
x_e = Content of more volatile fraction in reflux entering the plate, mol. per cent.
x_a = Content of more volatile fraction in overflow liquid, from the plate, mol. per cent.
x_m = Content of more volatile fraction in liquid on the plate, mol. per cent. A mean value lying between x_e and x_a.
X_c = Content of more volatile fraction in vapour under the plate, mol. per cent.
X_a = Content of more volatile fraction in vapour over the plate, mol. per cent.
X_a^z = Actual content of more volatile fraction in vapour over the plate, mol. per cent.
X_{th} = Content of more volatile fraction in vapour over the plate if it were in equilibrium with the liquid of x_m mol. per cent.
a = $X_a - X_c$.
b = $X_a^z - X_c$.
a^z = Maximum possible enrichment of vapour in passage through plate. This is $X_{th} - X_c$.
Q = Quantity of heat exchanged between vapour and liquid on a plate.
θ = Temperature change available for heat exchange Q.
r = Reflux ratio.
v_v = Vapour velocity based on free column cross-section.
η_i = Ideal efficiency.
η_r = Real efficiency.

* Paper received August 12th, 1935.

THE efficiency of a rectifying plate is ascertained by a comparison of the actually attained rectification on that plate with the rectification which is theoretically attainable. This theoretically best rectification can be found by means of a purely graphical method as shown in Fig. 1. On the equilibrium curve for a binary solution the so-called rectification line

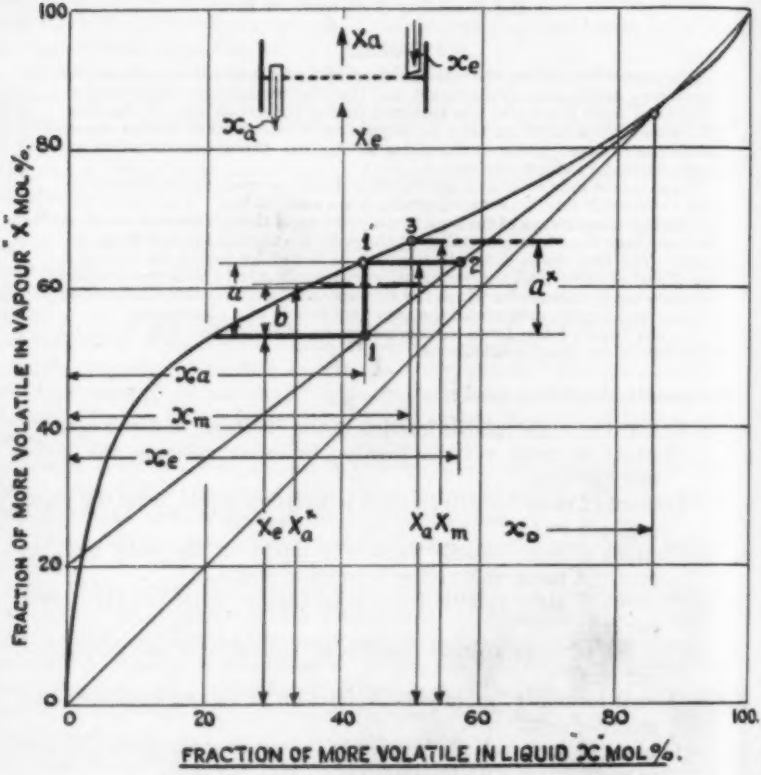


FIG. 1.

GRAPHICAL DETERMINATION OF THE EFFICIENCY OF A RECTIFICATION PLATE.

is drawn. The position of this line is determined by the content of the low-boiling-point fraction, x_D mol. per cent., in the distillate and the reflux ratio r of the column. The low-boiling-point content, x_a mol. per cent., in the reflux which flows away from the plate is related to a low-boiling-point mean content, X_e mol. per cent., in the vapour entering that particular plate as shown in point 1. The vapour rising from this plate is taken to leave the liquid with a content x mol. per cent. It has, as shown by the point 1', a content, X_a mol. per cent., with which is associated the

alcohol content x_e of the liquid flowing onto the plate. The ideal plate therefore obtains a rectification from X_e to X_a which is indicated by :

$$a = X_a - X_e$$

Actually the plate rectifies to X_a^x with enrichment of :

$$b = X_a^x - X_e$$

Then, from these two factors the efficiency is given as :

$$\eta_i = \frac{b}{a} \cdot 100 \text{ per cent.}$$

Numerous experiments which we have conducted indicate by direct measurement that an efficiency η_i can be given which is greater than

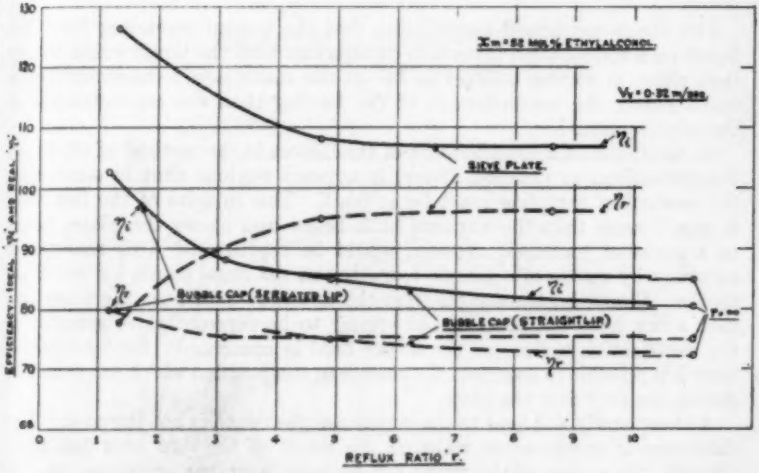

X = 82 MOL % ETHYLALCOHOL
V_L = 0·82 m/sec
SIEVE PLATE
BUBBLE CAP (SERRATED LIP)
BUBBLE CAP (STRAIGHT LIP)
EFFICIENCY : IDEAL, η_i AND REAL, η_r
REFLUX RATIO 'r'

FIG. 2.

RELATION BETWEEN IDEAL AND ACTUAL EFFICIENCIES AND THE REFLUX RATIO (ETHYL ALCOHOL–WATER MIXTURE).

100 per cent. This is impossible, as an efficiency of over 100 per cent. does not exist. Accordingly, there must in some manner be a discrepancy between the theory and the practice.

This difference lies in the generally assumed supposition that the vapour ascending from the plate is in phase equilibrium with the liquid leaving the plate. The liquid, however, flows onto the plate with a low-boiling fraction of x_e mol. per cent., and flows from the plate with a content of x mol. per cent. The mean concentration x_m on the plate must of necessity lie somewhere between x_e and x_a. The vapour which is in phase equilibrium with x_m has, in accordance with point 3, a content of X_{th} mol. per cent., so that the greatest attainable rectification is :

$$a^x = X_{th} - X_e$$

This equation gives a new efficiency η_r which is the actual or real efficiency. It is :

$$\eta_r = \frac{b}{a^x} \cdot 100 \text{ per cent.}$$

The ideal and the actual efficiencies consequently have different numerical values, and are in a certain ratio one to the other. This ratio is, above all other factors, dependent on the reflux ratio. Experiments conducted by Volland [1] with bubble-cap plates and sieve plates have demonstrated this fact. His results are given in Fig. 2, which shows the dependence of the ideal and actual efficiencies upon the reflux ratio r in the case of an ethyl alcohol–water mixture.

Plate Concentration Gradient.

The above-mentioned assumption, that the vapour ascending from the liquid on a rectification plate is in equilibrium with the liquid which leaves that plate, is correct only in so far as the mean liquid concentration is much nearer the concentration of the leaving than the concentration of the entering liquid.

As the result of a consideration of the factors in the method of efficiency determinations as detailed above, it appears obvious that in some way the method of sampling must be at fault. This in spite of the fact that it would seem that the vapours both below and above the plate, being in a state of turbulent motion, would be represented with reasonable accuracy by means of a sample extracted at the usual points by the usual means. Similarly, the sample from the downflow pipe onto the plate and that away from the plate would appear to be representative samples of the rectification action, so far as the fluid is concerned; for by suitable tests it is possible to ascertain the change in composition which has occurred during the flow over the plate.

A closer study will lead to the conclusion that such is not the case. The difference in temperature which is the result of the flow over the plate through the course of the rising hot vapours warrants consideration. It may be taken as a general rule that the temperature increase which occurs between the inlet downflow and the outlet downflow is of appreciable magnitude, and that the temperature gradient across the plate is such that the rate of rise of temperature is not a constant, but that it is varying as the liquid proceeds on its path. The rate of removal of the lower-boiling fraction would also vary, inasmuch as this also is a function of the temperature change. Hence it is logical to suppose that the rate of change of concentration of the liquid is not constant and that, in some way or other, the *rate* of removal of the low-boiling fraction is a function of the efficiency of the plate as distinct from the actual percentage of the fraction which is removed.

In order to investigate closely the concentration variation of a liquid during its run over the plate of a rectification column, a specially constructed plate of the dimensions shown in Fig. 3 was made. It was provided with one vapour throat, the interchangeable bubble caps having either straight or serrated lip as the occasion demanded. For the purpose

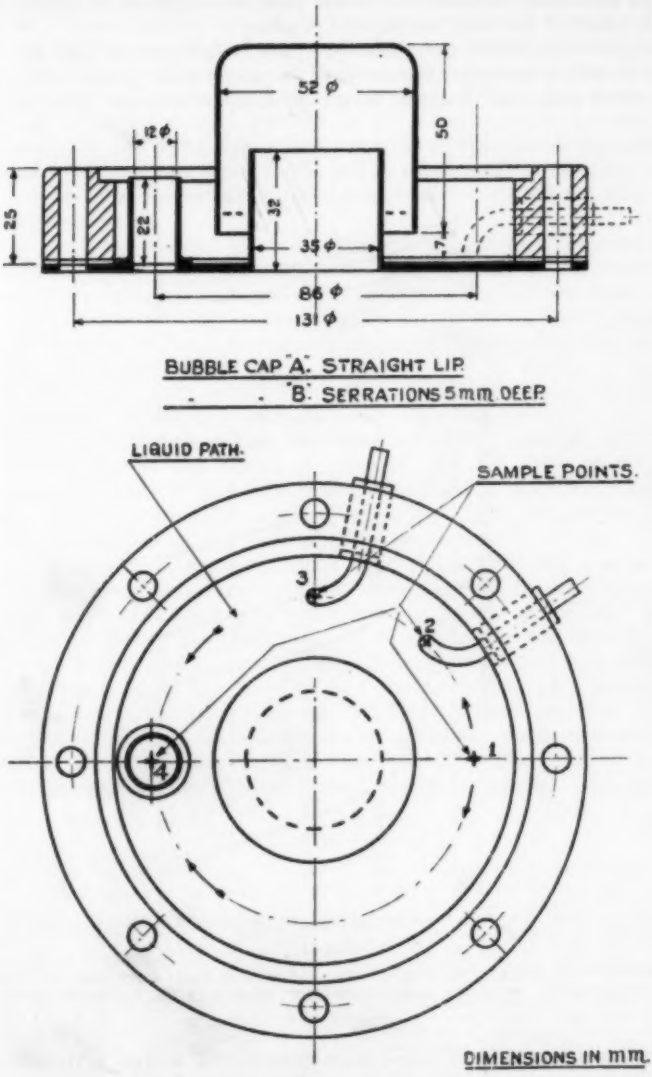


Fig. 3.

PRINCIPAL DIMENSIONS OF BUBBLE-CAP PLATE NO. 1 AND ARRANGEMENT OF SAMPLE POINTS.

of this and other research the bubble plate was enclosed in a column of which a part of the wall was entirely of glass.

Sample-taking tubes were inserted in the reflux pipes to and from the plate, as well as one under and one over the plate for the purpose of extracting vapour samples. Further, by means of tubes of 3-mm. bore, samples

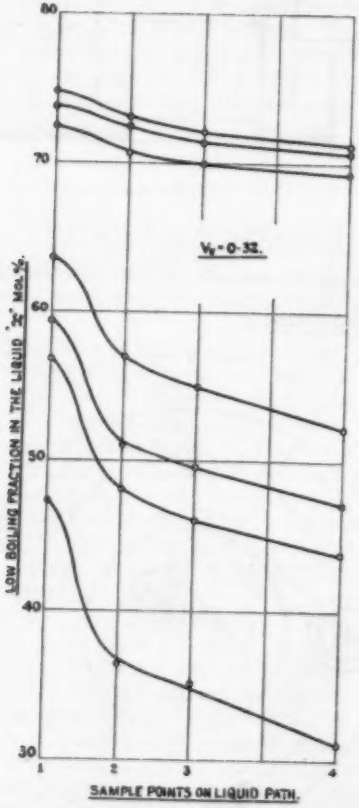


FIG. 4.

CONCENTRATION GRADIENTS FOR ETHYL ALCOHOL–WATER MIXTURES OF VARIOUS CONCENTRATIONS. BUBBLE CAP WITH STRAIGHT LIP, PLATE NO. 1. VAPOUR VELOCITY CONSTANT.

of the liquid were taken at two places spaced at 45° and at 90° respectively to a line connecting the centre of the reflux pipes. In this manner samples of the liquid were obtained at its entrance onto the plate, at one-quarter and one-half of the distance which had to be covered by the liquid during the course of its travel across the plate and at its exit into the downflow pipe. These points are indicated on Fig. 3 with the numerals 1, 2, 3, and 4 respectively. The tubes at points 2 and 3 were curved with the

inlet about 1 mm. above the plate, in order that the probability of the entrance of gas bubbles into them and thence into the sampling flask could be minimized. Should vapour find its way into the flask by such means, the liquid collected in the flasks would contain a higher content of the low-boiling fraction than the liquid on the plate. The inlets were so placed as to be exactly midway in the annular space between the bubble-cap lip and the column wall. It was assumed that this method of placing the sampling pipes would enable representative samples of the liquid to be collected at the various points, and it is believed that this object was attained.

By a particular method of valve control, which effected the closing of the downflow pipe onto the plate and the by-passing of the ascending vapour, it was possible to remove at any chosen instant the liquid contents of the plate. In this manner samples were obtained which provided a check on the calculated average concentration derived from the results given by the spaced test samples.

The fluids used were mixtures of ethyl alcohol and water in various concentrations. Working conditions were controlled and tests were run at different rates of vapour flow, the reflux ratio being changed as desired.

Test runs proved that during its progress over the plate the concentration of the liquid altered in a typical manner. This is shown by the curves in Fig. 4, in which the abscissa represents the liquid path travelled and the ordinate the alcohol content of the liquid in mol. per cent.

It will be seen that the concentration varies characteristically irrespective of the initial and final alcohol content of the liquid. At the commencement the slope of the curve is rapid, and the greater proportion of the concentration change has taken place by the time that the first quarter of the path is traversed. During this period the major exchange between the vapour and liquid has occurred, the contact which takes place over the second half of the path gives rise to relatively little exchange of the more volatile fraction. Each of the curves delineates the feature that the content of the low-boiling fraction decreases from the point of liquid entry at first rapidly, and then at a rate considerably slower. This change

TABLE I.

No.	V_g	r	x_D	L_0	L_m	x_m	V_m	V_0	b	a	a'	η_l	η_r
1	0·322	1·20	77·05	72·48	69·75	70·33	71·40	74·20	21·4	14·3	26·0	149·5	82·3
2	0·322	4·38	78·15	73·90	70·80	71·77	71·40	74·60	27·8	31·8	41·0	87·5	67·8
3	0·317	∞	76·60	74·65	71·10	72·35	71·40	74·95	35·8	43·5	51·0	82·3	43·6
4	0·318	∞	72·48	63·30	52·15	55·68	52·40	62·70	107·0	132·5	148·0	80·8	72·4
5	0·312	3·06	70·80	59·40	47·00	50·51	50·50	61·20	105·5	124·5	141·0	85·0	75·0
6	0·318	3·14	69·80	56·85	43·85	47·0	50·00	59·40	95·2	115·5	130·0	82·5	73·2
7	0·325	0·86	66·55	47·30	30·90	35·55	50·00	55·70	67·0	72·8	89·1	92·0	75·3
8	0·105	0·98	68·80	51·35	36·45	40·10	50·60	60·10	84·0	68·0	87·0	123·5	96·5
9	0·102	5·02	73·30	61·70	44·10	49·20	51·45	63·60	133·5	123·0	139·4	108·5	95·6
10	0·509	6·68	71·48	58·85	48·4	52·0	51·35	61·55	95·5	123·0	139·0	77·7	68·7
11	0·520	1·47	55·35	48·95	34·0	39·47	44·05	55·35	105·5	135·0	155·0	78·2	68·1
12	0·639	0·54	50·80	13·60	7·05	8·18	27·70	—	21·0	38·5	54·0	54·5	38·9
13	0·657	6·77	70·10	57·75	44·00	49·23	47·20	58·85	117·5	145·0	168·0	81·0	70·0
14	0·328	∞	73·2	65·00	54·33	57·50	54·33	64·35	103·0	121·5	136·6	85·0	75·6
15	0·321	3·16	71·47	60·35	49·20	52·49	53·75	62·52	86·5	98·3	115·0	88·0	75·2
16	0·310	1·19	68·35	53·25	37·70	45·57	51·56	59·76	81·3	88·3	108·8	102·6	74·8
17	0·314	∞	71·47	59·42	45·50	49·89	45·50	59·42	138·6	107·5	190·0	81·3	73·0
18	0·315	5·05	70·15	56·50	40·35	45·49	44·30	57·40	131·8	153·8	176·4	86·0	74·8
19	0·311	3·05	68·80	54·57	36·90	42·25	43·05	55·93	130·8	150·0	172·0	87·0	76·0
20	0·316	1·17	66·22	47·00	26·07	31·11	43·10	53·37	107·2	108·4	135·0	99·0	79·8

in rate of concentration influences very considerably the mean concentration of the liquid on the plate for any given operating conditions.

The actual mean value of x, *i.e.* x_m, can be ascertained when this curve is integrated, the value providing the basis for the calculation of the actual efficiency of the plate for the working conditions with which the curve was obtained.

Table I gives typical results when the ideal efficiency, in the usual manner, and the actual efficiency, based upon x_m, are calculated. Comparison of the two right-hand columns indicates that in each case the actual efficiency is less than 100 per cent., and that the irregularities present as ideal efficiencies no longer appear.

The column headings are :—

No. = Test run number.
V_v = Vapour Velocity, m/sec., based on free column cross-section.
r = Reflux Ratio.
x_D = Alcohol in distillate, mol. per cent.
L_e = Alcohol in liquid entering plate, mol. per cent.
L_u = Alcohol in liquid leaving plate, mol. per cent.
x_m = Alcohol in liquid on plate mean obtained from travel–concentration curve, mol. per cent.
V_u = Alcohol in vapour under the plate, mol. per cent.
V_o = Alcohol in vapour over the plate, mol. per cent.
b = Real rectification, based on liquid leaving plate.
a = Theoretical rectification, based on liquid leaving plate.
a' = Theoretical rectification, based on x_m.
η_i = Ideal efficiency, per cent.
η_r = Actual efficiency, per cent.

Effects of Plate Type on Concentration Gradient.

In Fig. 5 travel–concentration curves are given for two types of bubble caps, one having a straight lip and the other a serrated lip. The curves are of the same general type, and the comparison indicates clearly the superior "stripping" characteristic of the serrated lip.

The superiority of the serrated lip in this respect decreases where concentrations of greater strength are being processed until at about 80 mol. per cent. the concentration gradient given by the two types of bubble caps practically coincide.

The effect of varying the reflux ratio is shown in Fig. 6. As the liquid approaches the third sampling point, the slope of the curve decreases as the reflux ratio is lowered, other conditions, in particular that of the vapour velocity, remaining constant. This is attributable to the lower velocity of the liquid across the plate, such as is consistent with a lower reflux ratio, *i.e.* the longer period which any quantity of liquid remains subjected to the flow of a vapour stream of any particular concentration. The assumption leads to the conclusion that where the reflux ratio is high the length of the liquid path should be increased, as, for instance, by suitably designed and located baffles.

In order accurately to observe concentration variations in a rectifying column of commercial size a specially designed intermediate section was

built into a column used for the production of ethyl alcohol. The section was fitted with four glass-covered apertures spaced at 90° apart around the circumference. In each pair, one served as an observation glass, whilst the other diametrically opposite admitted light from an arc lamp. This arrangement enabled observations to be made on the effects produced on the liquid by various working conditions, and on the distribution of bubble activity over the entire plate. Principal dimensions of the plate are given on Fig. 7. Four sample points, similar to those already described, were built into the column.

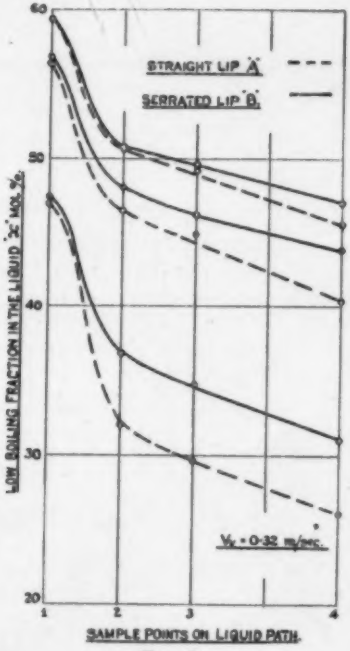


FIG. 5.

CONCENTRATION GRADIENTS FOR ETHYL ALCOHOL–WATER MIXTURES OF VARIOUS CONCENTRATIONS. COMPARISON BETWEEN STRIPPING CHARACTERISTICS OF BUBBLE CAPS WITH STRAIGHT AND SERRATED LIPS. BUBBLE-CAP PLATE NO. 1.

At the commencement of the test, curves were obtained of the type shown by Curve No. 2, Fig. 7. From these it appeared that in some way or other the fluid, after it had been stripped, became enriched by further travel. Investigation established the fact that the plate was not level on the axis at right angles to that joining the centres of the reflux inlet and overflow pipes. In consequence, the depth of liquid on one side of the plate exceeded that on the other, so that the bubble-cap lip was unequally immersed. The rising vapours naturally exhibited a tendency to flow more readily under that side of the lip which was higher, the combined effect of the difference in elevation and the smaller static liquid head

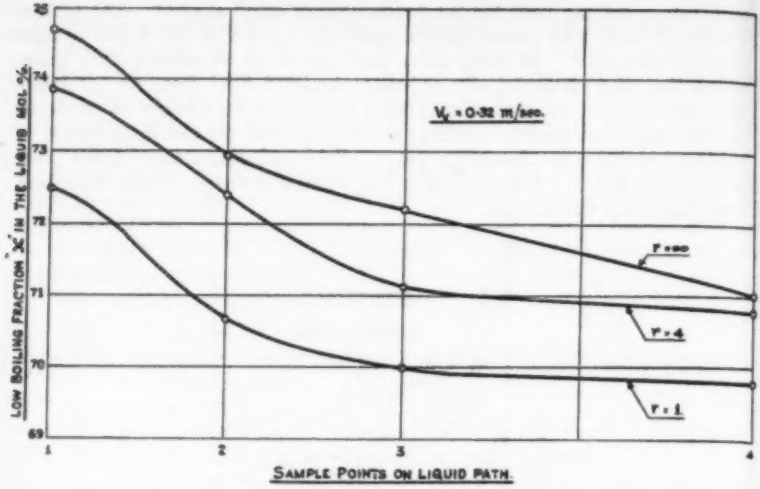


FIG. 6.

LIQUID CONCENTRATION GRADIENTS ON BUBBLE-CAP PLATE NO. 1 UNDER VARYING CONDITIONS OF REFLUX RATIO.

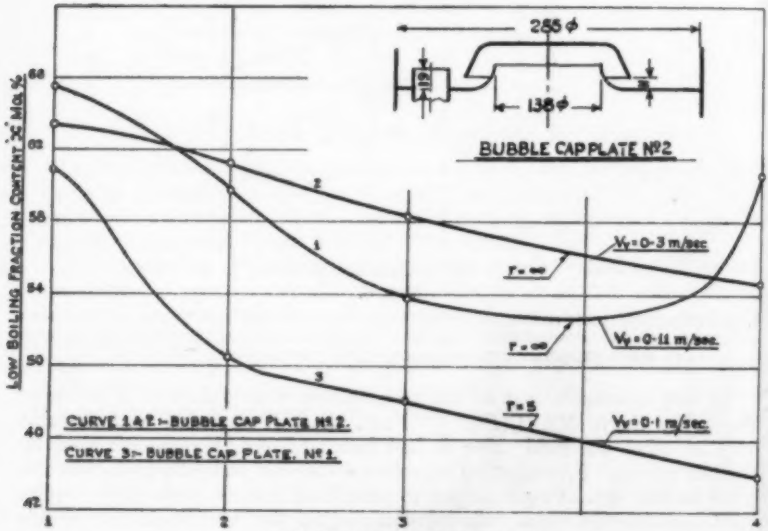

LOW BOILING FRACTION CONTENT 'X' MOL %
SAMPLE POINTS ON LIQUID PATH.
255 ϕ
138 ϕ
BUBBLE CAP PLATE Nº2
V_v = 0·3 m/sec
r = ∞
V_v = 0·11 m/sec
r = ∞
r = 5
V_v = 0·1 m/sec
CURVE 1 & 2 :- BUBBLE CAP PLATE Nº 2.
CURVE 3 :- BUBBLE CAP PLATE. Nº 1.

FIG. 7.

LIQUID CONCENTRATION GRADIENTS ON BUBBLE-CAP PLATES NOS. 1 AND 2. CURVE NO. 1 SHOWING EFFECT OF PLATE NOT BEING HORIZONTAL.

permitting easier vapour passage. Hence the liquid on this side was thoroughly agitated, whilst that on the other was hardly disturbed by the bubble flow; the two streams meeting at the overflow pipe gave a resulting mixture showing an increase in content of the low-boiling fraction as opposed to that of the stream from the upper side.

The total inclination of the plate was such that the difference in elevation of the points diametrically opposite was rather less than a millimetre. As this small difference in level gave rise to concentration differences in the two streams of liquid, emphasis is placed on the importance of the bubble plates being absolutely level.

Incorrect levelling produces uneven liquid disturbance to a greater degree where sieve plates are used. It was observed that with low vapour velocities it was quite impossible to arrange conditions so that an equal

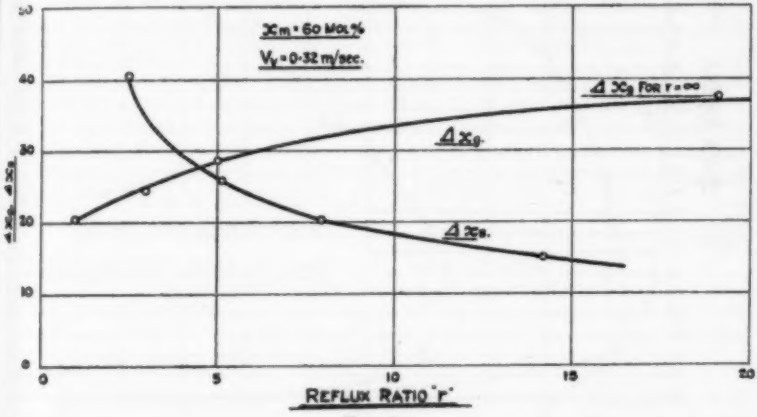


FIG. 8.

RELATION BETWEEN PERCENTAGE DIFFERENCES Δx_g AND Δx_s TO THE REFLUX RATIO.

distribution of vapour bubbles was maintained over the whole surface of the plate, although the plate could be precisely levelled by means of adjusting screws. To obtain efficient stripping it appears that some form of liquid-flow control must be exercised, in order that the fluid may be conducted over those sections of the plate through which the maximum and minimum quantities of vapour pass.

The unequal bubble distribution above mentioned will probably partly account for the differences which are found in the efficiencies of plates of large and small diameters respectively.

Liquid flow over a bubble-cap plate is to a certain extent directed and forced to keep to a definite path, so that the mean concentration of the liquid was easily ascertained by integrating the travel–concentration curve given as a result of analysis of samples taken at various points on the liquid path. The determination of the mean concentration of liquid on a sieve plate presented a difficulty which was solved in a satisfactory manner with the previously mentioned arrangement by which the rising

vapour could be diverted from under the plate, the reflux shut off and the liquid on the plate drained away and collected.

The difference between the mean concentration, x_m, and the concentration of the overflow was determined for both types of plates and expressed as a percentage proportion of the concentration change of the liquid due to its progress across the plate, *i.e.* $x_e - x_a$. In Fig. 8 these differences, designated Δx_g per cent. for the bubble-cap plate and Δx_s per cent. for the sieve plate, are plotted against the reflux ratio.

The slope tendency of the two curves is different. They throw light on

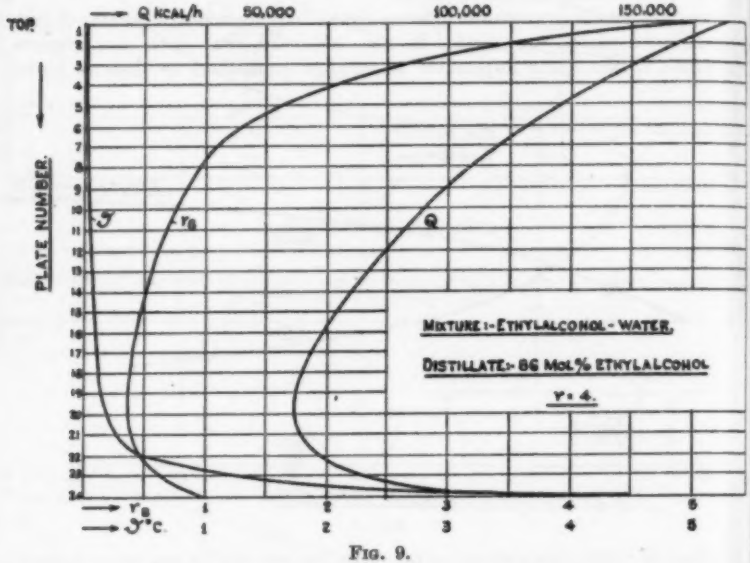


FIG. 9.

RELATION BETWEEN PLATE POSITION IN THE COLUMN AND TEMPERATURE DIFFERENCE ϑ, REFLUX RATIO r AND QUANTITY OF HEAT Q IN A COLUMN WITH EFFICIENTLY WORKING PLATES.

the actual efficiency as shown in Fig. 2 and its dependence on the reflux ratio. With smaller Δx_g and Δx_s the actual efficiency must become greater.

LIQUID–VAPOUR CONTACTS IN THE RECTIFICATION PROCESS.

The rectification process is, in itself, a heat-exchange process with which a material change is inherently connected. The numerical value for the quantity of heat exchanged, Q, provides the basis on which the dimensions of the rectification plate are calculated. An equation for the evaluation of Q has been deduced.[2] In Fig. 9 can be seen the magnitude of the limits within which the controlling factors change. Where the ordinate represents the number of plates in a rectification column operating

on an ethyl alcohol–water mixture the following functions are plotted as abscissæ :

θ = the temperature drop between the vapour and the liquid on a plate.
r_β = the plate reflux ratio.[2]
Q = the quantity of heat exchanged on a plate.

This column was working with a molar reflux ratio of 4, and was producing a distillate of 94 per cent. alcohol. The course of these curves, which show the three controlling factors for the efficiency of any one plate, demonstrates not only how the individual influences vary, but also why the efficiency varies from plate to plate. They also indicate the unreliability of any assumption that the plate efficiency is practically the same for all of the plates in a column. In spite of the course of the θ and Q curves, the rectification plates in a column invariably are made precisely similar in dimensions.

The controlling vapour velocity V_v gives rise to a relative liquid–vapour distribution on and above the plate which is of the greatest importance in the rectification process. This distribution originates and defines the specific liquid–vapour contact surfaces, and hence the particular heat and material exchange which occurs. Three phases of contact can be classified in which the vapour passes through :

(*a*) The liquid layer in form of bubbles of a distinct size and shape depending to a large extent on the design of plate.
(*b*) A foam or bubble layer floating on the liquid and
(*c*) A suspension of liquid drops which have been carried upwards from the foam layer by the explosive force of the breaking bubbles and the velocity of the vapour.

The distribution of these three phases is a matter of considerable practical interest and the photographs (see Figs. 10 to 16) indicate the various types of liquid–vapour distribution under the given conditions of reflux ratio and vapour velocity. Throughout these tests the liquid on the plate had a mean concentration of 60 mol. per cent. Plates of both bubble-cap and sieve types were used, the holes in the latter being of different diameter and spacing in each plate. The glass mantle surrounding the plates was 30 mm. high, so that the process could be readily observed and photographed.

On the left side of the glass mantle a piece of black paper was attached, the upper edge of which is level with the upper rim of the down flow-pipe.

The photographs show liquid–vapour distributions under various working conditions.

Figs. 10 and 11 were taken when the reflux ratio was 1·0 and the vapour velocities were 0·1 m./sec. and 0·5 m./sec. respectively.

The excessive turbulence due to the higher vapour velocity is obvious. The depth of the bubble layer is at least twice as great, while the bubbles are smaller and less regular in form. It is to be remarked that the level of the liquid layer is between 2 mm. and 3 mm. higher at the column wall. As the reflux ratio is the same in both cases, it is supposed that the bubble stream flows under the bubble-cap lip with such force that the liquid is

forced radially outwards, so increasing the level at the wall as opposed to that at the centre. In other words, the mean liquid–bubble layer interface assumes a concave form, and the time spent by the gas in contact with the liquid layer is correspondingly decreased. With such a short contact period it is certain that where a high vapour velocity is used this is a considerable factor in the lowering of the rectification efficiency.

At the vapour velocity of 0·1 m./sec. the size of the entrained drops is so small that they are not visible on the photograph. Actually the entire space above the bubble layer is filled with minute drops less than 0·5 mm. in diameter which are in continual motion. The much larger drops entrained at the higher velocity are readily visible.

Fig. 12 shows that the reflux ratio of infinity, *i.e.* when all the condensate was returned as reflux, has considerably altered the bubble layer, although the depth of the liquid layer is approximately the same as that in Fig. 11. The bubbles are much smaller and form a more compact mass.

The two photographs Figs. 13 and 14 show the influence of a very low and a high vapour velocity in the case of a sieve plate with holes of 1 mm. diameter spaced 7 mm. apart. At the lower velocity the bubbles are very large—about 8 mm. mean diameter—are quite regular in form, and rise slowly through the liquid and bubble layers. There is practically no entrainment. With a higher velocity the bubbles are small and irregular, and there is a violent turbulence. Here also the liquid level at the column wall is higher because the quantity of liquid entrained was such that the whole of the column inner surface 250 mm. above the plate was covered with a returning liquid film.

In Figs. 15 and 16 a sieve plate with holes of 2 mm. diameter spaced 10 mm. is operating with an infinite reflux ratio and vapour velocities of 0·3 m./sec. and 0·6 m./sec. respectively. In neither case can the liquid–bubble layer line be seen. This indicates that the available area presented by the 2-mm. holes for liquid passage to the next lower plate is too large, a factor which will have a considerable effect on the turbulence conditions and the height of the bubble layer.

The bubbles are very large, and with the 0·6 m./sec. vapour velocity a greater turbulence exists. A comparison with the photograph of the plate with 1-mm. diameter holes and a vapour velocity of 0·5 m./sec. shows that in the latter case a greater turbulence is attained. In fact, the appearance of the bubble layer is more suggestive of that of Fig. 13, where with the smaller holes there is a very low vapour velocity.

In each photograph the liquid–bubble layer interface is well below the upper edge of the strip of black paper. For every working condition investigated we found that the reflux did not flow over the downflow pipe rim in the manner of a liquid flood over a weir. It found its way into the downflow pipe in the form of bubble films and splash-drops. This condition was also observed in larger columns where, even with low vapour velocities, the liquid level was only about half-way between the plate and the rim of the downflow pipe. The first contact phase therefore appears to be diminished to such an extent that it is practically negligible.

Of the successive phases it is in the foam or bubble layer where the greatest effective contact area between liquid and vapour is to be found.

FIG. 10.

DISTRIBUTION OF LIQUID OVER A BELL-SHAPED BASE. DIAMETER OF COLUMN, 17 MM.; DIAMETER OF BELL, 52 MM.; HEIGHT OF FRONT, ABOUT 2 CM.; VELOCITY OF STEAM (CALCULATED ON THE CROSS-SECTION OF THE COLUMN), 0·1 M./SEC.; MIXTURE OF ETHYL ALCOHOL AND WATER; REFLUX RATIO, $v = 1$; ALCOHOL-CONTENT OF THE LIQUID, 60 MOL. PER CENT.

FIG. 11.

DISTRIBUTION OF LIQUID OVER A BELL-SHAPED BASE. REFLUX RATIO, $v = \infty$; STEAM VELOCITY, 0·5 M./SEC.; OTHER DETAILS AS FIG. 10.

FIG. 12.

DISTRIBUTION OF LIQUID OVER A BELL-SHAPED BASE. REFLUX RATIO, $v = \infty$; OTHER DETAILS AS FIG. 10.

FIG. 13.

DISTRIBUTION OF LIQUID OVER A PERFORATED BASE. STEAM VELOCITY, ABOUT 0·1 M./SEC.; REFLUX RATIO, $v = \infty$; MIXTURE OF ETHYL ALCOHOL AND WATER; ALCOHOL CONTENT OF THE LIQUID, 60 MOL. PER CENT.

[*To face p.* 816.

FIG. 16.

DISTRIBUTION OF LIQUID OVER A PERFORATED BASE. STEAM VELOCITY, 0·3 M./SEC.; OTHER DETAILS AS FIG. 13.

FIG. 15.

DISTRIBUTION OF LIQUID OVER A PERFORATED BASE. STEAM VELOCITY, 0·6 M./SEC.; REFLUX RATIO, $r = \infty$; OTHER DETAILS AS FIG. 13.

FIG. 14.

DISTRIBUTION OF LIQUID OVER A BELL-SHAPED BASE. STEAM VELOCITY, 0·5 M./SEC.; REFLUX RATIO, $r = 1$; OTHER DETAILS AS FIG. 10.

Consequently at this stage the maximum heat and material exchange takes place.

Our observations lead us to conclude that for both bubble-cap plates and sieve plates:

(*a*) The size of the bubbles decreases with increasing vapour velocity.

(*b*) With an increase in vapour velocity the depth of the bubble layer decreased.

(*c*) An increase in reflux ratio induced an increase in bubble layer depth.

(*d*) With a constant reflux ratio an increasing vapour velocity not only decreases the size of bubbles, but also appears to produce bubbles with a greater film thickness.

The above-mentioned effects of vapour velocity give definite characteristics to the actual efficiency–vapour velocity curves given in Fig. 17.

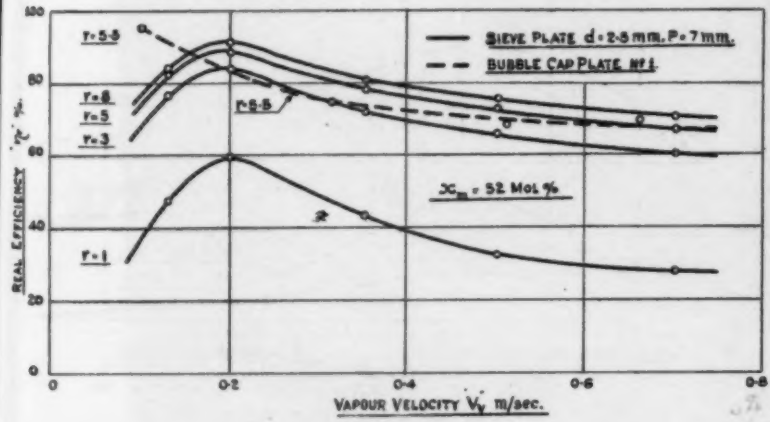


FIG. 17.

RELATION BETWEEN ACTUAL EFFICIENCY η_v AND THE VAPOUR VELOCITY v_v.

For a plate on which was mounted a cap with a straight lip the actual efficiency reaches a maximum at a vapour velocity somewhere in the neighbourhood of 0·1 m./sec. From this point it declines at first rapidly and then more slowly.

The sieve plate had holes 2·5 mm. diameter which were spaced 7 mm. apart. The η_v with a range of reflux ratios was found to be at a maximum when V_v was 0·2 m./sec., after which point it dropped in a manner similar to that of the bubble-cap plate. At velocities higher than this the disadvantages due to the short liquid–vapour contact time on the plate and the bubble layer of less depth become obvious. Until the velocity of 0·1 m./sec. is attained, it is also probable that the pressure difference in the vapour spaces over and under the plate is so small that the liquid

falls readily through the holes without undergoing that intimate liquid–vapour contact which is established at higher velocities.

Mixture Concentration and Plate Efficiency.

The general assumptions detailed above do not hold for all vapour velocities, and they are applicable to some ethyl alcohol–water mixtures in a modified manner. In order to investigate this aspect, the height of the bubble layer (together with that of the liquid layer) was ascertained

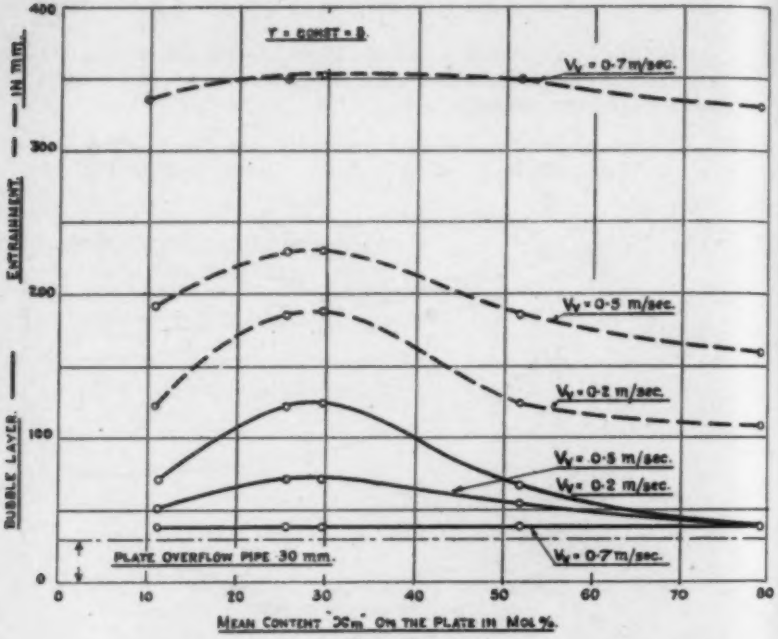

Y = CONST = 8.
V_y = 0·7 m/sec.
V_y = 0·5 m/sec.
V_y = 0·2 m/sec.
V_y = 0·5 m/sec.
V_y = 0·2 m/sec.
V_y = 0·7 m/sec.
PLATE OVERFLOW PIPE 30 mm.
BUBBLE LAYER — ENTRAINMENT — IN mm.
MEAN CONTENT "Om" ON THE PLATE IN Mol %.

Fig. 18.

Relation between height of bubble layer and entrainment and mean concentration of liquid on the plate.

when using liquids of different concentrations, the vapour velocity and reflux ratio being kept constant.

Results obtained with sieve plate are given in Fig. 18, which, at the same time, shows the height to which liquid drops of approximately 1 mm. diameter were carried. From these curves it appears that at a definite concentration the depth of the bubble layer is at a maximum. In the case of the ethyl alcohol–water mixture used, this lies at about 30 mol. per cent. In addition, the curves show that the depth of the bubble layer decreases with increasing vapour velocity. Ultimately at a vapour velocity of about 0·7 m./sec. the depth of the layer is dependent neither on the concentration of the liquid nor on the vapour velocity.

With a bubble layer thickness varying with the alcohol content of the liquid being processed, the plate efficiency can be expected to vary with liquid concentration. That this is so is shown by the curves in Fig. 19, where the optimum value of the efficiency of the sieve plate used is reached with a liquid of a concentration of about 40 mol. per cent. In this series of tests the vapour velocity was kept constant at 0·35 m./sec., and the curves demonstrate the efficacy of a rising reflux ratio throughout the whole range of liquid concentrations. With a definite content of the low-boiling-point fraction the depth of the bubble layer reaches a maximum, so giving rise to a correspondingly large liquid–vapour contact area. For rectification the essential factor is the quantity of heat, Q, exchanged between the vapour and the liquid on a plate, and the temperature decrease,

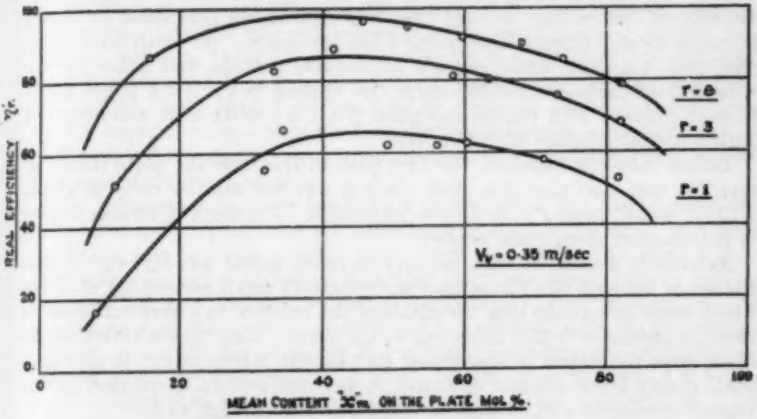


FIG. 19.

RELATION BETWEEN ACTUAL EFFICIENCY η_v AND THE MEAN CONCENTRATION x_m ON A PLATE. (SIEVE PLATE OF 107 MM. DIAMETER WITH HOLES OF 1·0 MM. DIAMETER SPACED 7·0 MM. APART.)

θ, available for this exchange. The smaller Q is for a completely working plate and the greater the temperature drop, the higher is the efficiency. This function accordingly increases as the ratio Q declines. The influence of the depth of the bubble layer and the ratio Q together produce the result that at a certain concentration the efficiency must be at a maximum.

ENTRAINMENT.

The third liquid–vapour contact phase—that in which the entrained liquid drops are carried up by, suspended in, or fall through the rising vapour—has decided effects on the efficiency of a column. Remarks regarding this phase will not be made here other than a few referring to the broken-line curves in Fig. 18.

Vapour rising with a given velocity will carry with it liquid drops of a given size to a given height. This height, due allowances being made for modifying factors such as the shape of the drop, the viscosity of the vapour,

etc., can be estimated fairly closely with the aid of formulæ deduced from Stokes' Law. A difficulty is encountered in the case of rectification columns because the vapour flow is not of the stream-line type. It is almost invariably turbulent. This gives rise to innumerable eddy currents, collisions between the liquid particles, etc., which disturb the kinematic conditions to such an extent that pure mathematical consideration is difficult. Nevertheless, the height to which drops of about 1 mm. in diameter were carried could be seen and measured in the apparatus with the glass mantle. From these observations the curves in Fig. 18 were plotted. They give the heights to which such drops were carried when liquids of various concentrations were used with different vapour velocities.

At normal operating vapour velocities the entire space within the glass mantle was filled with drops of varying sizes. Even with the low vapour velocity of 0·1 m./sec. a very fine mist-like cloud composed of liquid particles having minute dimensions filled the space. So small were these that they remained suspended for appreciable periods, and indicated the existence of turbulent conditions in the vapour flow. In a larger rectification column with bubble-cap plate No. 2 a similar mist was observed with a vapour velocity of 0·05 m./sec.

Taking into consideration the fact that in this case the plate diameter was 285 mm. and that the plate spacing was 500 mm., a ratio of about 1·75, it would appear it is almost impossible to prevent a certain degree of entrainment from plate to plate.

As already stated, at high velocity so much liquid was thrown up into the space between the plates that the relatively small percentage of drops which came in contact with the inside of the column wall were sufficient to create a stream of liquid returning to the plate. This factor undoubtedly diminishes the depth of the liquid and bubble layers owing to the proportionately large amount of liquid at any one instant suspended in the vapour stream as well as that flowing down the column wall.

The above article deals with some of the results of research undertaken in the Institute für Apparatebau of the Technische Hochschule, Karlsruhe. For their support and assistance particular thanks are due to the Helmholtz-Gesellschaft, the Deutsche Gesellschaft für Chemisches Apparatewesen, the Karlsruher Hochschulvereinigung and the Deutsche Reichmonopolverwaltung. Commercial apparatus was placed at our disposal by the firms: C. G. Bohm, Fredersdorf-Berlin and the Ges. f. Linde's Eismaschinen, Höllriegelskreuth.

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ASPECTS OF REFINING AND REFINERIES IN FRANCE.*

By X. Normand.

If I were to state that the history of petroleum refining in France began in 1928, after the voting by Parliament of the protection laws, I should risk offending a few of our white-haired refiners. It is true that we had in France petroleum factories—as they were then called in the neighbourhood—long before the beginning of this century, but in reality they were not of great importance, and the two old refineries which were running in 1928 only distilled between them a little over 300,000 tons of crude oil annually. To-day there are fifteen refineries, located mostly near the big ports; and they handle more than 6 million tons of crude oil annually. Benefiting by the experience gained in the large foreign refineries, and at the cost of continual improvements, they are as modern as is possible for installations averaging four years of age.

The refineries came into being at a period when the evolution of the petroleum industry all over the world was exceptionally rapid, and their operation was no sooner begun, than they were obliged to modify their production in order to follow, year by year, the alterations in quality imposed by new engine operation conditions. Furthermore, as the consumption of the various products did not coincide with the proportions already existing in the crude oil, it was found necessary, whilst decreasing refining costs, to contemplate a much higher operating rate for transforming units than that foreseen at the moment of the construction of the refineries.

This rapid effort at adaptation by the petroleum industry, which is not special to French refineries, seems to me unique in the history of the industry, and I will therefore try, as briefly as possible, to bring out its main features.

New Demands of the Market.

Until a few years ago, the French market was satisfied with three kinds of engine spirit:

Very volatile aviation spirit;
A light spirit, called "*Tourisme*," for motor-cars;
And finally, a heavy spirit, generally reserved for commercial vehicles.

To-day, there is a demand for seven types:

Three aviation spirits, two of which are currently sold, with octane numbers of 70 and 85 respectively, and a third, with an octane number

* Address delivered at the One Hundred and Seventy-first Meeting of the Institution of Petroleum Technologists, October 8th, 1936.

of 100, the manufacture of which has not yet been realized in France, but which is being claimed with insistence by the aviation industry.

Three light spirits for motor-cars, two of which have octane numbers of 60 and 75, whilst the third, called "*Tourisme speciale*," contains 12 per cent. of alcohol, and has an octane number of 65.

And finally, a spirit called "*Poids lourd*," which is a mixture of heavy spirit, with 25 per cent. of alcohol.

We will not recall the history of the "octane race," which, starting successively in America, England and France, is not yet finished to-day, but it will suffice to point out, in order to show its importance, that the power of the motor-car engine has been increased, in ten years, by 70 per cent. per cylinder cubic inch. Part of this increase is no doubt attributable to the increase in rotating speed, which has amounted to 30 per cent. during the same period; but it is primarily due to the improvement in the thermal yield of the engine the compression ratio of which has been continually raised by the marketing of spirit of increasing anti-knock qualities.

The average compression ratio of motor-car engines is at the moment 5·9 in France and 6·1 in the United States. On the other hand, as far as aviation engines are concerned, the situation is practically the same in all countries; the average compression ratio greatly exceeding six in all cases.

In spite of the continual progress made by the spark-ignition engine, it is definitely less efficient than the compression-ignition engine, and the number of the latter has increased to an extraordinary degree during the past years. At the moment, French refineries furnish fuel to about 20,000 compression-ignition lorries, without counting stationary engines and "rail cars," the number of which increases every month on our railways. To cope with this new demand for diesel oil, the refineries have not so far been forced to have recourse to very complicated methods, but they are aware that before long the "cetane race" may begin, and may necessitate the application of a new technique.

The engine manufacturers would not have been able to benefit by all the improvements, both from the mechanical and fuel points of view, if the refiners had not at the same time known how to increase the sources of high-quality lubricating oils. To cite just one example of the present severe conditions of lubrication, I would mention that in certain types of motor engines recently put on the market the average temperature of the oil in the crank-case is in the region of 150° C. (300° F.), whereas a few years ago it did not exceed 90° C. (200° F.). Aviation engines have still more severe lubricating conditions, and we are far from those days when castor oil appeared to be the ideal lubricant!

I will deal very rapidly with the other products, such as fuel oils, four qualities of which are at present sold in France, as against two a few years ago; but I must not fail to mention a striking—though indirect—tribute which has just been paid to the excellence of the road-repairing products manufactured by our refineries.

The average speed in 1936 of the victor of the "Round France" cycling race (a national event) was 31 km./hr., whilst our celebrated champions of the past—Faber and Petit-Breton—never exceeded 28 km. I do not

know if the cycling experts will agree with me, but I think that the improvement in this performance is due much more to the care taken in road-tarring than to the efficient pedalling of our cyclists.

Road oils, fuel oils, lubricating oils, 1936 spirits, are thus very far removed from their ancestors of 1926, and these improvements are the result of a complete renewal of refining methods during the same period.

Evolution of Refining Methods.

No sooner had the refineries been built than the refiners realized that their cracking plants, although they had been estimated on a liberal scale, would have to operate almost up to the maximum capacity, and that it would be necessary to increase reforming operations.

The decrease, in 1933, of the tax on heavy spirit (*poids lourd*), which, as already mentioned, is a blend of heavy spirit with 25 per cent. alcohol, gave the refineries a few months' respite. This admixture of alcohol gives the motor spirit an octane number in excess of 65 on the basis of heavy straight-run spirit of 45. Later on, and with the arrival in 1934 of Iraq crude, which to-day supplies many of the refineries, the latter were obliged to have recourse more and more to transformation operations. The octane number of light straight-run Iraq spirit is only 50.

If it be admitted that the French refineries are to-day well equipped for the production of motor spirit, thanks to the twenty-one cracking units the daily capacity of which totals 64,000 barrels, or 55 per cent. of the topping batteries, they are, nevertheless, unable to produce large quantities of anti-knock aviation spirit from the crude oils normally treated.

Cracked and reformed spirits are still prohibited for aviation. They maintain their old reputation of gumming the valves, which would seriously compromise safety during flight.

Up to now, in France only light cuts from a few special crudes have been made use of as aviation spirit. Consumption is still not very important, and, in order to obtain an octane number of 87—which generally is not exceeded—the addition of a few cubic centimetres of $PbEt_4$ per gallon only is needed. It would appear, however, that the improvements constantly being made in the chemical treatment of cracked spirits will shortly permit of their use for aviation. Refiners, too, are following with great attention the American experiments on the obtaining of *iso*-octane and *iso*-propylic ether which have led to the remarkable results already known.

In the case of the lubricating-oil industry, the use of selective solvents has enabled lubricants of high stability and with a viscosity index in the neighbourhood of 100 to be obtained from almost any crude.

The simultaneous chemical discovery of "dopes," such as paraflow, elektrion, chlor-ester and exanol, makes it possible to contemplate the lubrication of engines at extremes of temperature and pressure in a more efficient manner than hitherto, even when using the selected Pennsylvanian vintages.

Nevertheless, French refiners have not completely followed in the path of their American friends, and have not as yet introduced the hydrogenation processes borrowed from the related synthetic fuel industry. It is certainly possible to obtain, by means of this process, an additional yield of motor

spirit or lubricating oils; diesel oils and aviation spirit of exceptional quality, but very high construction and operating expenses are entailed. This is a consideration which the refiner, in common with other manufacturers, must take into account; for, though the consumer insists upon constant improvements in motor spirit, lubricating oils, road material and the like, he has in recent years only consented to pay about one-half of the prices which were in force ten years ago.*

It was therefore necessary for each refinery to reduce its costs, whilst adapting its products to the needs of the market. With this end in view, the most useful innovation in the technique of refining—which, fortunately, had been taken into account to some extent when building the refineries—has been the generalization in all branches of the continuous cycle.

The first battery of continuous distillation stills made its appearance about 50 years ago; but a detailed study was necessary of the influence of the concentration of reagents, and of the time of reaction in terms of the conditions of mixture, in order that the bulky, discontinuous, chemically-operating washers could be transformed into tiny centrifugal pumps. From that stage, it was then easy to combine counter-current, recyclage systems, etc., and all these methods, combined with the enormous increase in the efficiency of mixing, due to a decrease in the volumes handled, led to a substantial economy in reagents.

It is customary to utilize to-day from five to ten times less chemicals than hitherto. I have touched on the main reason above; but one should also take into account the recent evolution in methods arising out of a better understanding of the objects of the chemical purification of spirits.

There is no longer any question to-day of the almost total elimination of sulphur by destructive treatments, of which the least that can be said is that they usually threatened to eliminate at the same time the most anti-knock hydrocarbons.

All refiners have shifted their efforts towards softening treatments which transform the sulphur compounds in the raw spirits into odourless, non-corrosive products, leaving the hydrocarbons quite unaltered.

It is thus that the old soda plumbite treatment, abandoned for many years, has been re-adopted. It may later be replaced by alcoholic soda, cupric chloride, zinc oxide, or one of the numerous catalyzers now being tried. All these reagents have the advantage of easy regeneration by air, and only lose a few hundredth parts of their efficacity at each operation.

Work on the methods of using inhibitors is proceeding rapidly, and if their use could be generalized at an early date, an enormous step forward would have been made in the direction of reducing the cost of production of cracked spirits.

It was more difficult to subject lubricating oils to continuous treatment for such time as concentrated sulphuric acid remained the principal reagent. There were difficulties to be contended with in regard to the separation of the reaction products which the use of centrifugal methods did not always solve in a satisfactory manner. The process of refining by selected solvents has given a complete solution to the problem.

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* Leaving out of account taxes, which have, on the contrary, risen continually.

The installations in use in America permit of treatment by solvents of 50 per cent. of motor lubricating oils and special industrial oils. In France, there are at the moment three installations in operation: one using phenol, the second SO_2-benzole, and the third the Duosol process (propane and cresol [2]).

One refinery is further considering the use in the near future of the benzole–acetone process for the de-waxing of its oils.

Evolution in Refining Equipment.

The construction—mostly recent—of those plants for solvent refining of lubricating oils, the improvement of equipment, the chemical treatment of spirits, and the increase in the number of cracking and reforming units, have been the main features of the modernization of French refineries during the last few months. Fortunately, they were able to benefit by the important improvements made in such equipment all over the world, particularly during the prosperous years which preceded 1930.

At the present time plants occupy only about one-quarter of the surface covered hitherto. Distillation and cracking units have tall and slender outlines, and there is intense activity in the small chemical-treatment installations. The volume of raw material which each contains no longer corresponds, as in the past, to two or three times their daily treatment capacity, but only to the volume of a few hours, or even often of a few minutes.

In spite of the reduction in the enormous margin of raw material (which acted as a buffer), the regularity in operating continuity is much greater at present than before, as a result of the precision and flexibility of the measuring and regulating instruments which are now available. Thanks to the reliability which they ensure to the operation of the plants, and to the improvement in the steel of furnace tubes, it is now customary to operate for 100 days, with complete regularity, cracking runs which, a few years ago, could not have lasted for more than 100 hours, and the present-day units are, of course, of far greater capacity.

The 1936 operator, indeed, works his 30,000-barrel-per-day cracking unit with far greater security than did his colleague in 1913, with his cylindrical boiler, which cracked only 125 barrels, and the Anglo-Iranian topping unit of 60,000 barrels now in operation certainly gives no more trouble to the process superintendent at Abadan than does the 1000-barrel unit to the installation manager at Donges in Brittany.

In all probability, French refineries will never have to use such mammoths. The capacity of their biggest unit does not reach 15,000 barrels daily, but the number of their installations of all kinds is growing rapidly.

The beautiful French countryside, and particularly the peaceful banks of the Seine, lose a little of their calm and pleasant colouring, but the stress of modern times scarcely encourages Virgilian dreams. A nation which wishes to live must often sacrifice the peaceful oak to the factory chimney, and to-day the peasant, whether it be in Normany or in Provence, contemplates with less suspicion than he did five years ago the tall black or bright aluminium towers which form the usual silhouette of the refineries.

Are we destined to witness a further increase in the number of these

units? If we are to believe a recent American study, the tendency may rather be to develop distillation towards a closer separation of the constituents of petroleum than that followed at present, with a view to avoiding useless and costly reforming of certain hydrocarbons.

Or may it not be that the towers will disappear completely if the distillation process—always slightly destructive for the products—is one day replaced by a fractional separation of the different components by solution under pressure in natural gas condensates, as suggested by von Pilat?

We are, however, now in the realm of pure hypothesis, and no one can venture to-day to foresee the trend of the future. But it may well be that from your ranks, gentlemen, and from the work of your members, the mainsprings of future developments may arise. Your Institution, which we greatly admire in France, is now in the full force of maturity, having recently celebrated its coming-of-age. You have placed yourselves in the vanguard of scientific progress, and in the name of the French refiners, I tender you our best wishes for further success and the realization of your achievements.

THE EXHAUSTION OF PETROLEUM AND A DISCUSSION ON SUBSTITUTE FUELS.*

By A. de Boulard.†

Are we liable to be faced with a shortage of petroleum in the not far distant future? This is the alarming problem which arises, when we consider the continuous and rapid increase in the consumption of that product.

The motor vehicle is responsible for the major part of this consumption. When we contrast the enormous number of motor vehicles in use in the wealthy and civilized countries with the comparatively few vehicles in use in the impoverished and backward countries, we cannot help but be impressed by the potential motor-fuel requirements which would result from a world-wide spread of progress.

Periods of prosperity, characterized by all-round increases in consumption, are the periods when this problem receives the greatest amount of public attention. Production can scarcely keep pace with increased demand; reserve stocks dwindle rapidly. At such times it is the fashion for authoritative opinion to be loud in its warnings of the approaching end of petroleum. In actual fact the warnings that are needed are warnings against the prodigality inseparable from periods of prosperity.

I am not calling in question the wisdom of these warnings; but I should like us to examine whether such pessimism is really justified, and whether we need to apprehend the disappearance of our mechanized civilization through lack of fuel.

The Reserves of Petroleum.

The evaluation of the reserves of mineral deposits is an everyday operation. Applied to the various oil-bearing regions, it gives results which enable us to anticipate the maintenance of the present level of production for periods varying from ten to one hundred years; ten years in the case of countries where competition between producers is comparatively unrestricted, as in the United States; one hundred years in the case of countries where production is centred in a single producer, as in Mesopotamia. In the latter case development can proceed on rational lines.

Even so, this is a comparatively short period, but the industry knows well enough how short can be the active life of an oil-field, when the first discovery well is followed by intensive drilling. The peak of production is rapidly reached, and is followed by an accelerated decline. It must be definitely admitted that, for the world as a whole, approximately twenty

* Address delivered at One Hundred and Seventy-first Meeting of the Institution of Petroleum Technologists, October 8th, 1936.

† President of L'Association Française des Techniciens du Pétrole.

years' supply of petroleum is available. Petroleum must therefore be regarded as one of the minerals the depletion of which is most rapid.

Let us not, however, be unduly pessimistic.

In the first place, these estimates are based on the known petroliferous regions and on proved deposits. As soon as a new oil-field is opened up, geologists proceed to an intensive examination of the field. The geological structure is surveyed, the strata are classified, and a theory is constructed which serves for subsequent researches on the field. In this manner science sets a limit of depth to investigations. Experience, however, has shown that in the majority of fields new productive horizons have been discovered, when this artificial barrier of depth has been overcome, either by more enterprising exploitation, or as a consequence of improved drilling methods.

The extent of technical progress accomplished during the last few years is well known. Twenty years ago exploitation was carried out between 1500 and 3000 feet. At the present time petroleum is produced from depths greater than 6000 feet. A depth of 10,000 feet has been exceeded, and still deeper drilling is certainly possible.

If there is a limit below which petroleum cannot exist by reason of conditions of temperature and pressure, that limit is not yet known. Furthermore, many oil pools exist in buried structures, having been accumulated at earlier periods of sedimentation and earth-movement. Such structures require special methods of investigation, and the application of geophysical methods of exploration is one of the new lines of attack.

There therefore exists a hope of finding petroleum in all the continental masses, and the present distribution of the deposits, which seems to favour to an extraordinary degree certain countries like North America, is certainly not final. Discoveries in North America are due largely to the intensity of the search conducted without a break for half a century, whilst immense areas in other continents have not even been explored.

For these reasons there are, in my opinion, much greater prospects of finding larger reserves of petroleum than existing statistics would infer.

Theories of the Origin of Petroleum.

Efforts have been made to approach the problem from a different angle, by inquiries into the origin of petroleum. Due, however, to the fact that petroleum cannot be observed *in situ*, resort must be made to conjecture.

The most likely theory is that petroleum is of organic origin, representing the last stages of the transformation, by bacterial and reducing reactions, of the animal and vegetable substances carried into the sediments. It is not even necessary to admit, as for coal, an exceptional local concentration of these substances in a deltaic region. In the case of petroleum this concentration has occurred afterwards during migration, or by the distillation under the effect of internal heat, of the small quantities of organic substances—up to 5 per cent.—contained normally in all sediments. Thus the formation of petroleum may be a general process in the whole of the earth's sedimentary crust and petroleum, together with the bituminous shales and the natural gases, would represent the normal form of fossilized organic matter.

Were it possible to assume a mineral origin for oil, the limitations as to its possible occurrence would have to be still further reduced. There might be a possibility of oil generation which would resuscitate abandoned areas. Such suppositions are, however, very problematical.

Substitute Fuel.

We must now return to more tangible realities. Even if natural petroleum became too scarce, substitute fuels for the internal-combustion engine are known, and it would be necessary for us to develop them. It is this problem of substitute fuels which I would like to discuss.

In actual fact this problem is prominent at the present time not through fear of a general shortage of petroleum, but due to the desire of certain countries which are large consumers of petroleum products but deficient in natural resources, to render themselves as independent as possible of outside sources.

This problem obviously comprises an unlimited number of solutions in the immense realm of industrial chemistry; a few only have begun to be applied.

Above all, it is a question of cost of production. No artificial motor fuel will, from this point of view, for a long time be able to compete with the natural derivatives of petroleum. Hope is nevertheless permissible, for the result of technical progress is precisely that of lowering indefinitely the cost of production. The efforts made everywhere to produce synthetic motor fuels will, therefore, not be in vain.

In the first place, there is the artificial preparation of hydrocarbons analogous to petroleum. Chemically, a start can be made in this direction from every organic compound containing little or no oxygen. Naturally, the substances closely related to petroleum, such as coal, the lignites or the bituminous shales, have been considered first.

By low-temperature distillation tars are extracted, which may be transformed by cracking into motor spirit. There are some difficulties, and the yield is low. The hydrogenation processes, however, which are now an industrial proposition, permit the formation at will of such hydrocarbons as may be desired.

The conversion of coal, lignites and bituminous shales in these conditions already offers an immense field for the production of motor fuels. It is also possible to take as primary materials other vegetable hydrocarbon products, and particularly oils, so long as their price is not prohibitive.

Instead of seeking to obtain hydrocarbons identical with petroleum, there is nothing to prevent us (and it is much easier) obtaining other substances, provided they are liquid and capable of forming a motor-fuel mixture with air. That is the case, for example, with alcohols, and it would be the case with practically all analogous organic liquids.

The stumbling-block of all these processes is the quantity of energy at present wasted in obtaining the desired result; in the case of hydrogenation there is a loss of nearly four calories to recover one in the form of motor spirit.

The mode of preparation of fuel alcohols is to ferment, or treat chemically, vegetable materials specially cultivated for this purpose. The foregoing

objection no longer holds for the necessary energy is almost entirely obtained directly from the sun by the plant itself; moreover, the primary material is supplied in unlimited quantities, by the atmosphere and nature.

This process of manufacturing motor fuels, or rather of economic regeneration, is nevertheless costly on account of the charges for the labour necessary for cultivation, but it may be developed without limit, in theory. In practice, it has the drawback of requiring large areas of ground which will be required for the production of food as populations increase.

Other methods of fuelling motors, either directly with gases or with solid fuels through the intermediary of gas-generators mounted on the vehicles themselves, although recently improved, are not yet very practical, and they can scarcely be used yet except in certain particular cases. They are nevertheless available in emergency to make good a lack of petroleum.

It will not be beyond the powers of science to find other substitute fuels for the internal-combustion engine. So far from thinking that the latter may one day lack fuel, it is more probable that it will be replaced by a better means of producing mechanical energy, long before the exhaustion of the petroleum deposits. With its output of less than 30 per cent., even in the most favourable conditions, the internal-combustion engine is still a squanderer of energy.

SOME EXPERIMENTS ON MOLECULAR MANIFESTATIONS.

By Paul Woog, D.Sc.*

Molecular science has already given wonderful results, but its study presents tremendous difficulties.

Apart from the purely technical difficulties with which we have to deal, we have to realize that here, as everywhere else, the actual truth is undiscernible, and that we know only partial or temporary truths.

Besides, our mind is always inclined to simplify and generalize phenomena which are by themselves remarkably intricate. Therefore it is rash to assert that facts are just what we imagine them to be; but our schematic or simplified vision may be a necessary condition of success in research, for the aspect of reality itself would very often go beyond our understanding. We progress more safely if we restrict our vision, and avoid being dazzled. Otherwise, would not the discontinuities that we meet everywhere—quantas, electrons, mutations—prevent us from admiring the harmonious achievement of the world?

In the sphere of molecular physics too, it is very useful, for many a research, to reduce the intricacy of facts to a simplified form. From a philosophical and absolutely scientific point of view, we do this very reluctantly, but from a practical point of view we have the right to do it, provided that the fiction we have adopted is working usefully and that we do not lose sight of the weakness of our instrument.

In using the term "molecules" here, I shall purposely neglect all that belongs to the agitation which incessantly animates them—vibrations, oscillations, rotations—and shall consider molecules as particles looked upon at the instant when we might see them motionless.

Finally, I shall ask you to think of molecules not in the classical way in which they are usually regarded. Indeed, instead of admitting that the molecules of a body in its different phases—gaseous, liquid and solid—are identical, and that the direction and value of the attractive and repulsive power alone change according to the state of the body to which these molecules belong, I want you to consider the molecules of a body in the solid state, as if they possessed an actual stiffness, which stiffness will be missing in the molecules of a liquid body.

I set a high value on this supposition and I consider it quite rightful for, thanks to it, it is possible to offer a reasonable explanation of many problems of lubrication. Particularly in the very thin films which are formed upon surfaces, films that I have called "*Epilamens*," and on which depends oiliness, the mechanical resistance is always increased by the presence of solid molecules.

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It will now be of interest to consider some very simple experiments whereby one may observe the action of molecules and try to analyse their behaviour.

Experiments with Films.

I.—*The "Ice-breaker" Drop and the "Amœboid" Drop.*

Let us take a tray of about 50 cm. diameter and fill it with water; then let us form on its surface a solid tristearin epilamen. This may be done by putting some drops of a benzene solution of tristearin one by one on the water. The drops float on the surface, move, spread, and the solvent evaporates, leaving the glycerid molecules which float and direct themselves, so that the alcoholic and carboxyl parts of the molecule are immersed in the water, whilst the hydrocarbon chains stand up in the air. Thus, the water surface is covered with a very thin solid plate of tristearin. We know that the surface will be completely covered by the epilamen when the benzene solution no longer spreads, and keeps its state of a motionless lenticular disc.

Now let us put on such a prepared surface one drop of a fluid mineral oil containing unsaturated molecules—an ordinary spindle oil, for instance. We shall see the epilamen break suddenly, and straight-edged fissures develop in a wedge-like way and penetrate into the surface, pushing apart the two banks of the broken epilamen.

This movement is very much like the dislocation of an ice-field spurred by an ice-breaker boat.

The fissures are filled with mineral oil coming from the initial drop which runs out in a layer thick enough to allow the view of beautiful interference colours; also, if the lighting is sufficiently oblique, we can discern the level of the oil thread rising above the epilamen. The presence of the liquid oil can easily be discerned by sprinkling on the surface some particles of talc or lycopodium and blowing lightly: it is evident that these particles move only in the fissures, whilst they stay quite motionless on the solid epilamen.

What explanation can be offered for this phenomenon?

When we have placed the oil drop on the epilamen, the latter, being extremely thin, has not been able to bear the weight; tristearin molecules have then been diverted from the impact point, and the lower part of the drop has come in contact with the water. The drop then has a tendency to spread out with an energy function of the difference between its cohesion and its content of active atomic groups. It consequently forces back the obstacle formed by the epilamen molecules which surround it until the forces in play are reduced to equilibrium.

If instead of the spindle oil we use an oleic acid drop the molecules of which are all of high activity, a much more energetic effect is noticeable; as soon as it has been deposited the oleic acid drop goes directly through the epilamen and breaks it into a number of fissures spreading all over the surface. In this case, as the oleic acid forms a monomolecular layer, it is useful to powder the epilamen with particles before the addition of the acid in order to observe the phenomenon more easily.

An important point to be borne in mind at this stage is that the epilamen

resistance increases with the increase of the molecular volume of the elements constituting it, and can then be more easily wedged.

This phenomenon appears in our experiment. We have operated on a tristearin epilamen formed of big molecules, which therefore wedge themselves easily, set against each other and form an effective barrier which can only be pierced by a wedge.

If we repeat this experiment with a stearic acid epilamen consisting of molecules three times smaller than tristearin, the barrier will be less effective, and indeed an oleic acid drop (the spindle oil would not be active enough in this case) creates a narrow opening, generally circular, sometimes angular or polygonal, but always very small. In this case, molecules aggregating less energically move more easily and stick together, again allowing the invading liquid to spread until it has found its equilibrium.

Once more let us form a tristearin epilamen, and this time put down a saturated oil drop (vaseline oil) in which we have dissolved stearic acid. A very curious phenomenon then occurs: the drop flattens and without moving greatly it bubbles up on its edges and very quick movements of extension and contraction enliven it and make it look exactly like a small living animal. The drop moves in this way for a considerable time, sometimes throwing out "pseudopods," and then the movements gradually slacken and finally entirely cease.

Why does the oil drop adopt these amœba-like movements and this appearance of life?

As soon as it has been put down, the drop pierces the epilamen at the impact point, and comes in contact with the water; the active molecules of stearic acid which we have dissolved in the oil rush down towards the water, make contact with it and direct themselves towards the interface. On account of their strong attraction for water, new stearic acid molecules unceasingly reach the water, so that the bed of oriented stearic acid molecules will soon overflow the drop. This, thanks to the mutual affinity of the hydrocarbon chains, is drawn along and spreads. In stretching itself out, it grows thinner, and soon the stretched and flattened drop is entirely separated from the water by the accumulated layer of oriented stearic acid molecules "des-assimilated" by the drop, and lies upon this layer. The attraction of the sheet of water towards the drop is then suppressed, the range of the active forces between molecules approaching 10^{-7} to 10^{-8} centimetres, while the length of the hydrocarbon chains which bear the drop is here of about $24{\cdot}5 \times 10^{-8}$ cm. At this moment the cohesion forces are again predominant, and force the altered drop to contract quickly on itself—a movement which is now possible, for it occurs on the inactive extremity of the stearic acid molecules. Having finished its sliding movement along the bed of CH_2 groups, the drop, which has recovered its lenticular aspect, represents a bulk which can no longer be sustained by the stearic acid film; therefore it pierces it, and finds itself again in contact with water. Once more, the same phenomena will appear. In its contractive movement, the drop will certainly slide off the stearic acid molecules, for if we pour on the surface some particles of lycopodium, we shall see that those particles remain quite still at the very moment when the drop shrinks, whilst they are pushed again as soon as the drop again spreads itself over.

The cessation of the drop movements is caused by the progressive squeezing followed by the wedging of the epilamen molecules, which no longer allow the stearic acid molecules to be thrown up by the drop.

In addition, this experiment allows us to see the difference in the efficacy of the wedgings between small and big molecules. Indeed, if we form an "amœboid" drop, not on a tristearin epilamen, as before, but on a stearic acid epilamen, the molecules of this last substance being much smaller, the barrier they form is less efficient, and consequently the drop less under restraint lives a longer time.

Of course if we had operated on a liquid epilamen—of oleic acid, for instance—the phenomena of compression would have been so much diminished that the drop animation would not occur any longer.

Finally, if we put down a drop of oleic acid on any point of a tristearin epilamen when the "amœboid" drop moves, the very active molecules of oleic acid will produce such a compression of the epilamen that the "amœboid" drop will immediately be "suffocated" aloof, and will stop instantaneously, no longer retaining any trace of movement.

Outside its pseudo-physiological interest, the drop shows clearly part of the mechanism of oil lubrication, as in the two cases the slidings take place on CH_3 beds where the attractive fields are minima.

II.—*Molecular Magnitude and Film Behaviour.*

It will now be interesting to consider other means by which the difference existing between solid lubricating molecules and the liquid molecules may be determined.

The following experiments are based on the measurement of molecular dimensions. To effect these measurements we shall make use of the technique followed by Lord Rayleigh, Devaux, Langmuir, Adam and others, which is applicable to molecules lending themselves to orientation on the surface of water, *i.e.* polar molecules possessing an appreciable electric moment. We put on a pure water surface a certain quantity of molecules of bodies the molecular weights of which are known, and by means of a movable barrier we gather these molecules together until contact, which is shown by a suitable signal, and we measure the area covered by the molecules. The average statistical square section of the molecules is thus easily obtained; the square root of this section gives the width of the molecules, and the quotient of the molecular volume by the square section gives the height.

Now, we know that if the pressure is limited by the molecules' contact, the surface covered by a molecule is minimum for saturated molecules and notably higher for the homologous non-saturated molecules: indeed, the rigid saturated molecules orient themselves almost vertically on the water, whilst the non-saturated ones which are fluid flatten out on the water, where they are fixed by the double bond besides the terminal carboxyl: this being so, it is natural that the latter type of molecules occupy a larger area than the former. For instance:

Stearic acid	$22{\cdot}28 \times 10^{-16}$ sq. cm.
Oleic acid	$42{\cdot}6$ to $43{\cdot}3 \times 10^{-16}$ sq. cm.

We know also that if the lateral pressure on the epilamen were to grow bigger, the "double bonds," of which the adhesive energy for water is inferior to that of the carboxyls, would be driven out of the water, the hydrocarbon chains would then be completely elevated and the molecules, in spite of their fluidity, would only cover an area identical with that of the saturated molecules.

We operate with these stearic and oleic acid molecules, the dimensions of which are known, at the contact pressure.

If we successively put on the water a certain number of stearic acid molecules and then of oleic acid molecules, the surface covered by all these molecules is always exactly equal to the sum of the areas covered by each of these molecules taken separately. But if, on the contrary, we put on the water simultaneously a mixture of the two sorts of molecules which have previously been put into contact in a common solution or by fusion preceding the dissolution, we observe that the surface covered on the water is larger than the theoretical area. In our experiments this excess area was always observed, and it varied from 7·3 per cent. to 31·7 per cent. Thus, for instance 2,040,701 molecules of stearic acid and 1,928,006 molecules of oleic acid which ought to have covered 127·74 sq. cm., did in reality cover 168·25 sq. cm. in our experiment. There is therefore an excess area of 40·51 sq. cm.

Results of a similar nature are obtained if one uses other materials, such as mixtures of palmitic acid (solid) and oleic acid (liquid) or mixtures of stearic acid (solid) and trioleine (liquid).

The phenomenon can be explained as follows : When we place separately on the water the solid molecules and the fluid ones, each one of these molecules when arriving on the water surface can orient itself freely according to its nature, and it is to be expected that the sum of the areas of all the molecules present should be equal to the total of the areas of each individual molecule.

But if the solid and liquid molecules are brought into contact before the forces of orientation on the water have had the opportunity to act, some molecules are drawn together in accordance with their mutual affinity : the carboxyls attract each other, and the hydrocarbon chains, the mutual affinity of which is also notable, come into very close contact.

When we put a drop of the mixture on the water surface, these molecular associates come in contact with water, and the orientation of each element occurs. At this moment the double bond, which has come near the water owing to the liquid state of the molecule which contains it and to the corresponding sinking of the chain which is the immediate consequence, is attracted by the water surface and draws, together with its own chain, one or more chains of solid saturated molecules which are contiguous to it, and which from this moment also sink to the water, taking up more room than before.

This interpretation is confirmed by the following fact. The solid bodies that we have employed in these experiments are formed by molecules of relatively small section. Now, the flexibility of a material varies in inverse ratio to its section : it was therefore to be expected that the larger their transverse dimensions, the better the molecules would resist the tendency to sink. That is exactly what we observe if we repeat these

experiments with a triglyceride the molecule of which, composed of three linked molecules of acid, is more undeformable than are the molecules of these acids taken separately. For instance, if we operate on tristearin molecules (the section of which is $66{\cdot}9 \times 10^{-16}$ sq. cm.), these rigid and resistant molecules are not only no longer drawn along, but it is worthy of remark that, on the contrary, they straighten out the fluid molecules, and here we observe a total area inferior to the theoretical calculated surface. This reduction amounted to about 15 per cent. in our experiments.

It is evident from these simple experiments that it is possible to bend or straighten molecules spread out in a single layer, and that the ordinary laws of mechanics can be applied to the constitutive particles of the epilamens. It can readily be realized, therefore, how important is the choice of the molecules which play the essential part in the phenomenon of lubrication.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Seventy-first General Meeting of the Institution of Petroleum Technologists was held at the Rooms of the Chemical Society, Burlington House, London, W.1, on Thursday, October 8th, 1936, Dr. F. B. Thole, Vice-President, in the Chair.

THE CHAIRMAN, in opening the meeting, apologized for the absence of the President, Sir John Cadman, who to his very great regret was unable to attend owing to other very urgent business. Sir John particularly regretted his absence because the present evening was the opening meeting of a new Session in which a very important event in international petroleum circles would take place—namely, the Second World Petroleum Congress. The great success of the First Congress of that name was still fresh in the members' minds, and there were already signs that the Second Congress would attain, and perhaps even excel, the high standard of the First. It was particularly appropriate in these circumstances that, at this first meeting of the new Session, the members had the pleasure of welcoming two colleagues from France who were playing a very important rôle in petroleum affairs in that country. M. de Boulard was the President of l'Association Française des Techniciens du Pétrole and, on behalf of the members of the Institution, he desired M. de Boulard on his return to his country to convey to their French colleagues their most sincere good wishes to their Association. (Applause.) They would all regret that Dr. Woog had been prevented by indisposition from being present. Before M. de Boulard presented his address he was sure the members would be very pleased if M. de Boulard could spare a few moments to tell them something about the forthcoming Second World Petroleum Congress.

M. DE BOULARD said he desired first of all to convey to the meeting the greetings of his own Association, which he had the honour and great pleasure of representing that evening. He saw in such an exchange of visits and views a proof of the growing friendship among the members of the two Institutions, and of the necessity of maintaining between them a most intimate contact. The occasion of the Second World Petroleum Congress next year would be the very best of all occasions to make this contact still closer. As a member of the Congress Committee he was very pleased to state that the organization of the Congress was progressing in a very satisfactory manner. The French Foreign Office had agreed, at the Committee's request, to send to some forty Governments of other countries an invitation to send official delegates to the Congress. Several Ministers of the French Government were honouring the Congress with their patron-

age. Outside France many of the important oil interests of the world had readily agreed to assist the Committee in the work of organization. Several national committees were at present actively engaged in organizing the technical participation of their countries.

It was not necessary for him to say to what extent the Committee appreciated the help which it had received from the very beginning from the Institution of Petroleum Technologists. It was far from an easy task to prepare a Congress during which all the questions relating to the oil industry would be carefully examined, but the Committee felt extremely confident about it all by knowing to what extent they could count on the help and goodwill of the oil technologists of the world, and more particularly those of Great Britain. French petroleum technologists desired their English colleagues to join with them in Paris for the Congress in as great numbers as possible, and to contribute papers on any of the questions indicated on the programme.

The following papers were then read :

" The Exhaustion of Petroleum and a Discussion of Substitute Fuels," by A. de Boulard.*

" Aspects of Refining and Refineries in France," by X. Normand.†

DISCUSSION.

THE CHAIRMAN, in opening the Discussion, said that the members that evening had had the privilege of observing two well-known men of science thinking ahead into the future and, judging from the facts at present available to them and to others, planning and prophesying what developments they anticipated in the future. It seemed to him that M. de Boulard's review very accurately and very clearly summed up the position of the future as regarded fuels in general. That summing up amounted to this—that our reserves of fuel, actual, and potential, gave no cause of fear whatever provided they were produced and used intelligently. From time to time, of course, the nature of the fuel demanded would change. One foresaw, even at the present moment, the time when heavy oil would become in greater and greater demand, exceeding the demand for gasoline; but there was no reason to doubt, from past experience, that the chemist and the engineer between them would always be able to transmute the less desired and the less convenient material to the more convenient; to convert, for example, raw coal into de-ashed powder, into hydrocarbon oils, or into gas; to convert one form of oil into any more desirable form; and, in due course, as M. de Boulard had indicated, quite possibly the aid of the biochemist would be called upon in order to convert atmospheric carbon dioxide chemically into combustible gases or into combustible liquids.

MR. E. A. EVANS said that he well remembered Sir William Ramsay some 20 years ago suggesting that the coal supplies of this country would last only for about another 20 years, but there was still plenty of coal in this

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* See pp. 827–830.

† See pp. 821–826.

country—in fact, it was hard work to sell it; and he thought it was quite likely that there would be sufficient oil for all motor-cars in 20 years' time, when they would be wanted even more than they were wanted now. After all, when the present supplies which were under-ground were exhausted, there would still be the shale.

The Chairman has referred to the advances made in connection with fuel. Also one could not help but admire the work which had been done in connection with the advancement of lubricating oils, but when they were told that the temperature of the lubricating oil used to be considered to be quite a normal figure at 90° C., and that now it was 150° C., he was inclined to doubt that statement. He did not think anything like temperatures of 150° C. were obtained. He knew that in America it was stated that cars there hurtled along hundreds of miles after hundreds of miles at 85 miles an hour, and it was quite possible for the oil to rise to a temperature of 150° C. If that were so, it was purely a question of economics—whether it was cheaper to use more oil or whether it was cheaper to have better cooling; but he could not imagine a motor-car running with its oil temperature at 150° C. for a very long period, particularly when it was realized, as had been discovered at Cambridge recently, that it was probable that the surface temperature of the molecules on the bearing rose to something like 1000° C. It was a little difficult to imagine that oil at 150° C. was going to be sufficiently stable to maintain the proper bearing insulation.

If he was not trespassing on the time of the meeting, he would like to refer to what had been happening in America with a copper–lead bearing. It has been stated that the fatty acids and the fatty oil were definitely dangerous to the copper–lead bearing, but one found now that that view had been entirely discarded, because somebody had realized that it was not the fatty oil after all but that it was the bearing itself. These matters had to be looked upon with a proper perspective.

Reference had been made to the use of "dopes." There one came back to the subject of research. Dopes had come to stay—it did not matter in what form, paraflow, inhibitors, or anything else. It was a sign of the times. Another change of view was the attitude towards the elimination of sulphur from petroleum products. It had been stated over and over again that sulphur products were the absolute enemy of the engine. Yet now one went to the other extreme and put sulphur compounds in to raise the film rupture strength of oils.

Mr. A. Beeby Thompson thought that very few would disagree with the conclusions reached by M. de Boulard. All those associated with oil-field work realized that all their original calculations as to reserves of oil had been very erroneous. In reality, no oil-field in the world, with the possible exception of the limestone fields, was ever exhausted. All that happened was that it ceased to be developed further because it could not be worked economically. Every oil-field had a new life if the price of oil rose. One could refer to innumerable oil-fields where the original conclusions had been wrong. Taking Trinidad, for instance, he himself with others had very carefully mapped the anticlines and, as they had thought, the oil-fields. Now, those fields were all developing down the synclines, and some of the best wells had been discovered in the middle of the anticline on ground

which the original geologists had most carefully avoided in all their work. The same thing has occurred in Burma. One of the latest developments there had occurred at a spot which for many years the operators had very carefully avoided. Therefore he felt sure that there was no cause for any alarm. With prudence and technique they could all look forward to a long life in many of those oil-fields which had been prophesied to be coming to an end long, long ago.

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